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THE 1998 DEXTER AWARD ADDRESS

"FROM AN INSTRUMENT OF WAR TO AN INSTRUMENT OF THE LABORATORY: THE AFFINITIES CERTAINLY DO NOT CHANGE"
CHEMISTS AND THE DEVELOPMENT OF MUNITIONS, 1785-1885

Seymour H. Mauskopf, Duke University

I am deeply pleased and honored to be this year's recipient of the Dexter Award. I might add that I was also somewhat taken aback when I was informed that I had been nominated, for I recognize that I have been something of a "prodigal son" regarding the history of chemistry. I left the field for about fifteen years to co-author a book with my life-long friend (and chair of this session) on a subject very different from the history of chemistry (1). Moreover, my research in the field has been somewhat unorthodox; I have sought out topics that have seemed interesting to me but had not attracted much scholarly attention, at least at the time I began my study. And the focus of these topics has been less on chemistry per se than on the interaction between chemistry and other domains of the physical sciences. It was therefore all the more heartening to have my research honored in this most signal way.

The quotation in the title of my talk, which I have also used as the epigraph of one of my publications, is taken from the "Cinquième mémoire sur la poudre à canon (2)" of Joseph-Louis Proust. It is important that I honor Proust by the use of one of his quotations because he has played an important role in the trajectory of my own research in the history of chemistry. Originally, I was interested in the aspect of his work for which he is best known—analytical chemistry and the Law of Definite Proportions—but with the unusual context of the relationship of Proust's Law to the concept of fixed mineral species in contemporary French crystallography and mineralogy. My orientation was traditional and "internalist" (to use the terminology of the time). Although I was led to give some attention to social and institutional contexts of Proust's career when I wrote my biographical essay on him for the Dictionary of Scientific Biography, I was still quite firmly focused on the Law of Definite Proportions there. For example, I remember quite well looking over...
quickly—and passing by—nine late and lengthy publications by Proust on “poudre à canon.” However, while researching the DSB essay, I had secured a copy of two sets of lectures Proust had delivered during the years he spent in Spain (1785-1806), and datable internally to the first years of the nineteenth century. These lectures were the basis of my return to the history of chemistry in the 1980s. My orientation was now much more attuned to the context—one might say the problematic—of Proust as a practicing chemist in Spain, a backwater for chemistry throughout the eighteenth century. This led me to turn to Proust’s applied chemistry, particularly his military chemistry, for he had been invited to Spain in 1785 to teach chemistry to the cadets of the Royal Artillery School in Segovia. After re-examining Proust’s lectures, I noted that three or four of fifty lectures per set had been devoted to the chemistry of gunpowder. This caused me to return, with renewed interest, to his nine articles on “poudre à canon.” The result was my article, “Chemistry and Cannon,” published in Technology and Culture (3). The new focus on the chemistry of gunpowder led me back to Lavoisier and eighteenth-century chemical and physical analysis of gunpowder and its explosive reaction and, more recently, forward through the nineteenth century. A stay at the Beckman Center for the History of Chemistry helped me to initiate these studies, and grants from the Hagley Museum and the National Science Foundation have enabled me to pursue them in the interstices of a busy teaching and administrative schedule.

When I began my studies in the 1980s, I found the recent scholarly literature on the development of munitions and, particularly, on the role of scientists in this development, to be sparse, to say the least. There was, of course, Partington’s classic A History of Greek Fire and Gunpowder (4). But, as the title implies, this book concentrates on the medieval and early modern period; it has very little to say about post-1700 developments. Another important study for the early modern period, if more distantly related to my focus, was Hall’s Ballistics in the Seventeenth Century (5). But for the more recent period, there was a virtual absence of scholarship, the honorable exceptions proving the rule by their small number. These include Multhauf’s study of Lavoisier’s attempt to deal with the late eighteenth-century French problem of saltpeter supply (6) and Gillispie’s discussion of Lavoisier’s role in the Régie des Poudres, the French gunpowder administration, in his magisterial treatise (7).

In the past decade or so, the scholarly situation has improved noticeably. Steele has made an important contribution to the study of ballistics in the eighteenth century, centering around the mathematician and ballistics expert, Benjamin Robins (8). Bret has been producing comprehensive studies of the organizational changes in the French gunpowder administration and technical improvements in gunpowder making during the late eighteenth and early nineteenth century, giving particular attention to the role of chemists and scientific training (9). The inception of something like a coherent research group on the history of gunpowder is symptomized by the recent sessions devoted to it at the biannual meetings of ICOHTEC (10) and organized by Dr. Brenda Buchanan. One result was the publication of the first modern set of studies on gunpowder (11).

If a start has been made in the study of eighteenth- and early nineteenth-century munitions centering on gunpowder, the same can hardly yet be said about the development of organic high explosives in the later nineteenth and twentieth centuries. There have been two dissertations on the early development of smokeless powder but neither has been published (12). Studies by two of today’s participants, Richard Rice, on Mendeleev and Russian munitions, and Jeffrey Johnson (and Roy MacLeod) on armaments on the eve of World War I, should initiate a sophisticated historical literature on this period.

The general historical problematic behind my studies of munitions is the question of how science and craft intersected—and came together—between the last quarter of the eighteenth and the last quarter of the nineteenth centuries. The subject of munitions is, of course, part of a much more general problematic concerning the science and technology of materials in this critical era. My historical studies of munitions have focused on their use as military propellants, as opposed to other military uses (as fuses, rockets, explosive shells, etc.) or civilian uses. The traditional military propellant was gunpowder—"black powder"—the ancient mixture of saltpeter, sulfur, and charcoal. Although other, more explosive materials (like potassium chlorate) were considered as military propellants from time to time, the first really serious rival to gunpowder was “guncotton,” a highly nitrated form of cellulose, made by treating cotton with concentrated nitric and sulfuric acid, discovered by Christian Friedrich Schönbein in 1846 (13). Nitrocellulose was to have a great and varied industrial future in the nineteenth and twentieth centuries (14), but what most notably attracted Schönbein’s and his contempo-
rareys’ attention was the explosive property of guncotton. It was, weight for weight, more powerful than gunpowder and burned completely without producing smoke and, apparently, without fouling guns. Yet it took forty years to develop an effective nitrocellulose-based smokeless powder as a military propellant. What I want to focus on is a part of that story: the work of the English munitions chemist, Frederick Abel, who tried to “tame” guncotton for use as a military propellant in the 1860s. Abel achieved part of this objective by 1865 and appeared to be very optimistic about developing a smokeless military propellant from guncotton that would replace gunpowder; he abruptly abandoned this research in the late 1860s and instead embarked on a massive study of the function of gunpowder in guns of all calibers.

What follows is a “systemic” approach that I have found to be of heuristic value in conceptualizing the relationship of science to the development of military propellants (15). Of the three such systems (two “physical” and one “social”) I shall focus on gunpowder to illustrate the physical systems.

I. The Systems

The first system is that of the propellants themselves. It includes the physical and chemical properties relevant to their functions as military propellants. In the case of gunpowder, it was through the pneumatic chemical discoveries and the general reconceptualization of chemical substances and reactions during the Chemical Revolution that the first approximation to the modern understanding of the chemistry of gunpowder came about. There was initial optimism that chemical understanding itself would lead fairly directly to improved gunpowder. But by the first part of the nineteenth century, it became apparent that physical characteristics of gunpowder—the size, shape and density of powder grains, the manner in which wood was converted into charcoal, the way in which the three components were “incorporated” together—were at least as important as purely chemical considerations in determining the way gunpowder functioned. “Function” here is relational. So my second system is the relation between the propellant and the instrumental complex in which it operates, in this case, of course, the guns and their projectiles (bullets, cannon balls and shells). Here a number of different issues arose. One was whether military propellants functioned the same way in field guns as they did in laboratory test tubes. The issue is brought out well in Proust’s epigraph: “From and instrument of war to an instrument of the laboratory, the affinities certainly do not change.” Proust, more than any other chemist, attempted to develop gunpowder chemistry into a useful military application; the context of the quotation was his assertion that the saturation proportion between charcoal and saltpeter, determined in the laboratory, was precisely the same as that in a gun (16).

Another issue concerned the relationship of changes in the propellant to guns and projectiles (and vice versa). It was the introduction of an English-derived powerful gunpowder into France in the early 1820s, which was soon blasting test cannon out of commission, that led French investigators to concentrate on studying the physical parameters of gunpowder in order to control its ballistic force. By the late 1850s, attention was turned to major changes in all aspects of guns: the materials out of which they were made, the mechanism of loading and, above all, their power. It now became more important than ever to determine and control the rate at which the ballistic force of the propellant was released and built up in gun bores. Although French investigators had been moving towards this recognition earlier in the century, it was an American, T. J. Rodman, who seems to have been the first to determine the relationship between powder grain (or cartridge) size, burn rate, and gun bore pressure. What enabled Rodman to come to his insight was his invention of an ingenious device, the Rodman gauge, to measure pressure as the projectile moved down the gun bore under the impulse of gunpowder explosion. Rodman also made important improvements in cannon casting and was particularly concerned with controlling pressure in his large, smooth-bore “columbiad” cannon. The Rodman gauge and Rodman’s general principle, that the size and shape of powder grains had to be adapted to the caliber of the gun in which they were used, were rapidly accepted throughout Europe (17).

In 1857, at almost exactly the same time that Rodman was developing practical means of measuring and controlling gun bore pressure, a more theoretical and laboratory-based advance in determining explosion pressure and other physical parameters was being made in Germany. Its authors were the chemist Robert Bunsen and the Russian artillerist and munitions chemist, Leon Schischkoff. The basis of their determination was an unprecedentedly detailed analysis of the products of gunpowder explosion and a calorimetric measurement of the heat produced from it. From this data, they applied thermochemical considerations, only then recently
come into use, to determine the temperature of the explosion and, from that, the pressure and the theoretical work (18). Neither Bunsen nor Schischkoff developed this research further, but it was hailed as "the model for all subsequent research on this subject (19)," and taken by all munitions investigators as the watershed in the scientific understanding of explosion and detonation.

The two systems outlined so far have dealt with the physical materials of military propellants and their relationship to guns and projectiles. However, there is one other system to which I would like to give some attention: that dealing with the social contexts of the scientific investigators themselves and the nature and "style" of their investigations. It would involve such parameters as national scientific tradition, scientific and technological formation, motivation for investigation, patronage/employment, and relationship to the military propellant manufacture. My renewed and reoriented interest in Proust was focused on these parameters, and I have since extended my purview to the French, English, and American investigative traditions in the eighteenth and nineteenth centuries. This third system is illustrated with a brief overview of the development of munitions research in France and England in these centuries.

With the appointment of Lavoisier in 1775 as one of the four régisseurs des poudres and de facto chief of the Régie des poudres, the reformed French gunpowder administration, scientists were introduced into the industry as they had already been in other industries such as dyeing and metallurgy (20). Until then, gunpowder making was a craft in France and elsewhere; the detailed rules for gunpowder production and testing that had been laid down in France in 1686 were, to the best of my knowledge, generated without scientific input. Although Lavoisier's best known activity as a régisseur was his attempt to develop saltpeter production, he also instituted tests concerning many aspects of gunpowder production: which wood source produced the best charcoal for gunpowder; which process of trituration and incorporation (stamping mills or edge runner wheels) was best, etc. (21). He also instituted what Gillispie has termed "scientific administration (22)." This included the scientific training of all future commissaires des poudres, the directors of French powder mills. One recipient of this training was E. I. Dupont.

The institutionalization of science in the French gunpowder administration survived the vicissitudes of French politics throughout the nineteenth century. However, there ensued something of a disciplinary dialectic in the investigative tradition concerning munitions in the course of this century. During the French Revolution, chemists were in its forefront; but the Napoleonic regime ordained that all gunpowder administrators be graduates of the École polytechnique. From that time through the Franco-Prussian War the primary disciplinary orientation was physical rather than chemical, even though such distinguished chemists as Gay-Lussac and Pêlouze served on the Comité consultatif of the powder administration, established soon after the Restoration (23). I would suggest that this change in research orientation represented the intersection of two systems in my mode of analysis: the physical system of propellant and gun (the crisis engendered by the introduction of a new type of more powerful powder ca. 1820, mentioned earlier) and, in the social system of the scientific investigator, the requirement of an École polytechnique background in military engineering. It should also be mentioned that contemporary American munitions investigators, such as Rodman, received analogous training at West Point and carried out research in a style similar to that of the polytechniciens.

The period after the Franco-Prussian War was marked by the collaborative activities of the chemist, Marcellin Berthelot, with the polytechniciens, Émile Sarrau and Paul Vieille. This great trio of French investigators brought the chemical and the physical traditions into synthesis through the union of thermodynamics and thermochemistry, in part because of the pioneering paper of Bunsen and Schischkoff. It should be noted that munitions production and research were solely a state activity and, for much of the century, under the administrative control of the Ministry of War (24).

In England there appears to have been no comparably coherent tradition of institutionalized scientific involvement in munitions prior to the appearance on the scene of Frederick Abel (1827-1902). A charter student (and one of the most esteemed) of W. A. Hofmann at the Royal College of Chemistry, Abel left the college in 1851 to take a post as Demonstrator of Chemistry at St. Bartholomew's Hospital, London. Two years later he secured the position of Lecturer in Chemistry at the Royal Military Academy, Woolwich, upon the retirement of Faraday. Founded in 1741 to train cadets in artillery and engineering, the Royal Military Academy had instituted a scientific and technical curriculum in the 1770s and had some distinguished faculty, such as the mathematician and ballistics expert, Charles Hutton; but, to the best of my knowledge, Faraday was the first Profes-
sor of Chemistry. Faraday had delivered an annual course of lectures on chemistry and related subjects to the cadets from 1830 to 1851 (25). Abel moved to the Woolwich Arsenal and soon began to carve out a new professional niche in munitions as Scientific Advisor to the War Office (1854), a position soon elevated to "Chemist of the War Department (26)."

When Abel moved to Woolwich, "there was some uncertainty as to his duties (27)." There did exist a Royal Laboratory at Woolwich dating back to the seventeenth century (28), in which, after 1783, the manufacture of military powder at the government powder mills was supervised (29). In the late eighteenth and early nineteenth centuries, experiments very similar to the contemporary ones of Lavoisier and Proust were carried out at the Royal Laboratory under the direction of William Congreve (1743-1814) to ameliorate the quality of gunpowder, which had sunk to a deplorable level (30). In the words of Congreve's student (31):

Through his systematic practical research into the manufacture of gunpowder and his ability to enact change Congreve had transformed British powder from one of notorious quality to a world standard.

The French certainly shared this positive view of British powder in the post-Napoleonic period. However, it does not appear that the investigative activities at the Royal Laboratory were pursued after Waterloo. I certainly know of nothing in England before the late 1850s comparable to the investigative tradition of the French polytechniciens of the period.

The early 1850s were certainly propitious for a scientist to develop a career in munitions. Abel had scarcely settled into his position when the post-Napoleonic détente gave way to the Crimean War. In this first multinational war in forty years, the changes in artillery were very apparent, as the opening lines of the official report of an American military observer testified (32):

The introduction of the long gun to fire shells horizontally, both for land and sea service, with a tendency to increase the calibers; and of the rifle, with various modifications for all small arms, may now be considered as the settled policy and practice of all the military powers of Europe. (Moreover), an attempt is being made by several of the European powers to adopt the rifle principle to the heaviest artillery.

These changes "spurred England into action...to revolutionize the whole field of artillery (33)" during the rest of Abel's career.

Institutional changes in the British military establishment also began in the mid-1850s with the establishment of a consolidated War Department. By the late 1850s, the continued tumultuous international scene, combined with concern over the rapid changes in artillery, led to the enlargement of the facilities of the governmental powder mills at Waltham Abbey (34) and to the establishment of ongoing committees to investigate both the new guns and their ammunition requirements: in 1858, the Ordnance Select Committee, subcommittees of which studied gunpowder and guncotton; and, in 1869, a Committee on Gunpowder and Explosive Substances (35). Abel either served directly on the committee, as he did on the Committee on Gunpowder and Explosives throughout its existence, or he served in an advisory capacity as Chemist of the War Department.
II. Abel and Guncotton

Abel described his entry into the field of guncotton (36):

Early in 1863, by desire of the Secretary of State for War, I entered upon a detailed investigation of the manufacture of guncotton, the composition of the material when produced upon an extensive scale, its behavior under circumstances favourable to its change, and other subjects relating to the chemical history of this remarkable body.

When Abel took up the investigation of guncotton as a military propellant, it had already sustained almost two decades of a very checkered history since its discovery in 1846. News of favorable behavior in the field was mixed with reports of disastrous explosions at production sites, leading to prohibition of manufacturing and testing. The question of the stability of guncotton was thus of the utmost practical importance. A few years after Schönbein's discovery, and after most governments had abandoned the investigation of guncotton for military use and had even banned its production, a method of producing what promised to be a pure and stable guncotton was developed by an Austrian artillery officer, Wilhelm Von Lenk. Von Lenk refined each step in the procedure for making guncotton: he used rovings of cotton (long skeins of yarn for textile manufacture) as the basic material, which he steeped in a mixture of the strongest commercial nitric and sulfuric acid for forty eight hours. After a preliminary cleansing, the modified yarn was subjected to a running water bath (in a stream) for at least three weeks, dried, and finally immersed in a weak solution of potash and water-glass (37). The resultant product appeared to be remarkably uniform and stable (38). In 1853, Von Lenk obtained leave from the Austrian government to establish a factory for the production of guncotton. Although opposed by some artillerists, Von Lenk succeeded, by the early 1860s, in securing the right to manufacture guncotton in Austria and for the adoption of guncotton into the Austrian artillery service. It was at this moment, when "...it was considered as definitively settled that Gun-cotton would before long be introduced into the service in place of gunpowder, for artillery purposes (39)," that the Austrian government permitted Von Lenk to communicate his method to the British (40). Although the British had their own earlier experience with a major explosion at a guncotton factory, they were impressed with Von Lenk's improved guncotton and the promise it afforded to replace gunpowder (41). Von Lenk himself came to England in 1863 to report on his procedure to a blue-ribbon committee of the British Association for the Advancement of Science (BAAS). Production was begun by Messrs. Thomas Prentice and Co. of Stowmarket.

Despite favorable reports like the one from the BAAS committee, studies in France and elsewhere challenged the claims about safety and stability of Von Lenk's guncotton. In fact, there was an explosion at the Stowmarket factory soon after production of guncotton commenced (42). As a result of these positive and negative developments, Abel took up the study of guncotton and, in the mid 1860s, performed the most comprehensive and detailed experiments up to that time. Initially, he shared the optimism of the BAAS committee about the feasibility of substituting guncotton for gunpowder.

In terms of my mode of analysis, there were challenges facing the adoption of guncotton as a military propellant that pertained both to its material nature and to its function in the system of propellant and gun. Abel's research was primarily focused on the first of these challenges. It involved considerations of the chemical nature of the material and of the means to promote and insure purity and stability. Although it was recognized early on that nitrocellulose was formed by a process of nitration with the release of water, and that higher degrees of nitration produced more explosive materials, there was great uncertainty and considerable controversy as to how many chemical varieties of nitrocellulose existed and how stable they were. This last issue was obviously of special importance for guncotton. In England it had become accepted that there were three forms of nitrocellulose, corresponding to the introduction of one, two, or three units of nitration in the cellulose. Guncotton, the most highly nitrated form, was in fact trinitrocellulose. The three forms were distinguishable by their differential solubilities in ether-alcohol mixtures. However, this analysis was challenged on the continent, and Paul Vieille could write as late as the early 1880s, shortly before he developed Poudre B (43):

Very different formulae have been suggested to represent the composition of the nitro-products derived from celluloses, and particularly the composition of products of maximum and minimum nitration. These products were, moreover, obtained by processes differing at the same time both as to temperature of reaction, concentration of acids, and the nature of the sulfo-nitric mixture employed. Therefore the results were not susceptible of any general interpretation.

Abel subscribed to the English chemical view of nitrocellulose and satisfied himself that Von Lenk's procedure produced a distinct and stable chemical substance, trinitrocellulose. But this view (and the stability of Von Lenk's product) had been challenged by a number of
continental researchers, the most formidable of whom was the French chemist, Jules Pélouze, whose analysis of guncotton signaled a lower level of nitration than that indicated by Abel’s formula for trinitrocellulose (44). Abel argued that the results obtained by Pélouze were the outcome of incomplete nitration of the cotton, either because of an insufficient period of acid digestion, the use of too weak an acid or an insufficient amount of acid, or choice of a low quality cotton. As an *experimentum crucis*, Abel showed that subjecting the less highly nitrated cellulose to a second acid digestion raised its weight to the level Abel had obtained for guncotton. At that level, the product was far more stable than the French and others had claimed. Nevertheless, Abel discovered, was the presence of partially oxidized organic impurities present in the cotton. It was the decomposition of these to which Abel assigned the cause of the instability even in Von Lenk’s product. To remove these impurities, Abel recommended a final washing of guncotton with an alkaline carbonate.

Even more important than the chemistry was a physical procedure instituted by Abel: pulping the cotton before nitration “according to the method commonly employed for converting rags into paper (46).” Because of the tubular structure of cotton fiber, impurities survived even the most rigorous washings; by destroying this capillary structure and agitating the pulp in a large volume of slightly alkaline solution, an exceptionally pure and stable guncotton was obtained. Abel’s pulping procedure became standard for the rest of the century. Moreover, if immersed in water or impregnated with moisture, guncotton seemed all but indestructible and certainly safer to handle and transport than gunpowder.

The question of guncotton’s stability was very important but only a part of the larger issue of whether guncotton could be substituted for gunpowder as a mili-

The apparatus of Bunsen and Schischkoff from “On the Chemical Theory of Gunpowder”

Abel admitted that even he had not achieved complete nitration; there was always a small residue of lower-level nitrocellulose products. It was to these that the French attributed guncotton’s dangerous instability, especially upon exposure to light and heat. Abel, in fact, found the very opposite; indeed, the addition of dilute collodion (a less highly nitrated cellulose than guncotton) actually seemed to promote stability “probably because the fibres are partially sealed, or in some other way mechanically protected (45).” Of more concern,
tary propellant (47). In the mid 1860s, that certainly remained the desideratum of military study of the material. But, regarding the functioning of guncotton in the field, the main problem was the rapidity and force of guncotton detonation. Von Lenk had attempted to control its rate of burn by twisting skeins of guncotton around hollow wooden cylinders. Although at first very promising (48), this soon proved to be ineffective in guns (49). However, the development of the pulping process and of procedures to dilute guncotton with more inert substances (e.g. less highly nitrated forms of nitrocellulose or even cotton) (50) seemed to offer new possibilities for controlling the force of guncotton by converting the pulp by pressure into solid masses of any suitable form or density, as was done with gunpowder (51):

Some results, which are admitted by the most sceptical as encouraging, have already been arrived at, in the systematic course of experiments which are in progress, with the object of applying the methods of regulation...to the reduction of guncotton to a safe form for artillery purposes. Its arrangement in a form suitable for small arms is a much less difficult problem, which may be considered as approaching a perfect solution.

This optimistic scenario for guncotton as a military propellant was taken from the second talk Abel presented to the members of the Royal Institution in 1866. There is a third in this series entitled “On the More Important Substitutes for Gunpowder,” given in May, 1872. The disheartening mood of this one regarding guncotton is sounded in the opening line (52):

No progress has been made since 1868 in the application of explosive agents, other than gunpowder, to artillery purposes.

Abel noted that even the very promising cartridges for small arms sporting guns were “wanting much in uniformity” although they were free from smoke and gun fouling (53). He did suggest an improvement: compressing guncotton pulp under pressure and impregnating the compressed mass with an inert material such as paraffin, stearine, or india rubber to control the speed and violence of detonation. This had been successfully tested in small arms and rifles but “the experiments upon this system of preparing cartridges have not been pursued for the last four years (54).” Abel also mentioned a guncotton diluted with sugar and saltpeter which had shown “considerable success” in “repeated trials,” and “Shultze powder,” devised by a Prussian artillery officer in the mid 1860s by nitrating wood shavings or sawdust and mixing the result with saltpeter. However, Abel characterized this latter as an “imperfect kind of gun-cotton,” that was “scarcely bidding fair to compete in uniformity of action with the excellent gunpowder now manufactured for breech-loading rifles (55).”

By 1868, then, Abel seems effectively to have ceased experimentation on guncotton as a substitute propellant for gunpowder. Research did continue for developing other military uses, for example, in bursting shells, torpedoes, and blasting agents. What had caused him to abandon so precipitously a research topic that had looked so promising? Such accounts as there are of Abel’s research claim that he abandoned research on guncotton because he was unable to get it under complete control, especially concerning its rate and temperature of burning (56). Although this is true enough, I doubt that this alone explains Abel’s abrupt cessation of research. However, Abel himself gave an explanation in a comprehensive account on munitions and explosives research delivered to the British Association for the Advancement of Science in 1871 (57):

A very decided advance had been made towards the successful employment of guncotton in field guns before the Government Committee on Guncotton ceased to exist in 1868; and if the experiments on this subject, which were then suspended, as well as those relating to the employment of guncotton in military small arms, have not been resumed, it is only because the Committee on Explosives, to whom the further investigation of these matters has been entrusted, has hitherto been fully occupied with the more immediate important investigations relating to gunpowder.
Under the auspices of this committee, Abel himself had returned to focus his research on gunpowder. Over a decade, starting in 1868, in tandem with Andrew Noble, a polymath in gunnery and munitions, Abel pursued research on the function of gunpowder in guns of all calibers that was the most comprehensive ever carried out (58).

The context for Abel’s return to gunpowder research lay in the developments of the decade before, associated with T.J. Rodman and with Bunsen and Schischkoff. These offered researchers unprecedented opportunities to understand and control both interior and exterior ballistics through the determination, measurement, and control of the ballistic force of gunpowder explosion. Guided by the scientific paradigm of Bunsen and Schischkoff and employing Rodman’s gun bore pressure data and an improved version of his pressure gauge (the crusher gauge), Noble and Abel carried out systematic and comprehensive chemical and physical tests. As Abel himself stated (59):

Well, at about the time that Rodman was working at this subject in America, and Bunsen in Germany, we English, once more bestirred ourselves in this matter, and set to work in earnest to improve gunpowder, and to advance the knowledge regarding its action and the conditions to be fulfilled for bringing its force under better control.

In order to overcome the challenge of approximating field conditions of a large gun bore in the laboratory, the investigators made use of an “explosion apparatus” designed by Noble. They also did comparative tests in guns of all calibers to tabulate the total work realized per lb. of powder for every gun, charge, and description of powder in the English service. From this tabulation, it was possible to deduce the velocity of any standard projectile in any standard large gun (60). As for the practical impact of their work (61):

The results of their [Noble and Abel] labours, as time went on, was to produce much slower-burning forms of gunpowder than those which had found favour in 1870 and earlier. The production of these new types of powder characterized by gradual combustion exercised a far-reaching influence over what came to be regarded as the correct form of built-up gun construction.

In the evaluation of technological change, there is, I think, a natural tendency to read backwards from some ex post facto state of affairs. In this case, it would be the supplanting of gunpowder by a guncotton-based military smokeless powder. In fact, this began in the mid-1880s after the first one, "poudre B," was developed by Paul Vieille. By the end of the decade, variants (sometimes with nitroglycerine as well as guncotton) had been devised in all European countries and in the United States. Abel himself came out of retirement to devise one of the best, “cordite,” in collaboration with James Dewar. The age of gunpowder gave way to that of high-explosive, smokeless powder. But in the late 1860s, gunpowder itself was very much a technology undergoing transformation and improvement. Abel’s disparagement of Schultze’s powder in comparison with “the excellent gunpowder now manufactured for breech-loading rifles” certainly indicates that Abel saw gunpowder in this light. Therefore, to interpret Abel’s abandonment of guncotton research as simply a case of failure to control it as a military propellant is to miss the real advances that had been and were being made in its principal competitor, guncotton, in its systemic relationship to changes in gunnery. Although gunpowder did lack the attractive feature of smokelessness, these advances had made it superior to guncotton in most other ways. Corroboration for this view is found in a popular lecture by Abel on "gun cotton" in 1873 (62):

Gun cotton can be made more controllable for small arm purposes, but we have not yet been able to tame it sufficiently to allow of its being used with any degree of confidence in great guns. The attempts made up to the present time to moderate its action have only been partially successful in the smallest cannon, and there appears no prospect whatever of our taming it sufficiently for use in larger guns. I have here a diagram representing different kinds of gunpowder now in use, and here are also specimens of the different descriptions used for heavy artillery. Twenty years ago these small grains of powder represented the cannon powder in universal use. Then we began to build larger guns, and after some time this larger-grained powder was introduced as a safer powder to use in such guns. Powder burns rapidly in proportion to the size and density of its grains or masses, and the fine powder was found to act injuriously upon the big guns, although we had then only got up to the 100-pounder Armstrong gun. We considered we had taken a great stride when we passed from that small grain to this larger grain; but rapid progress was made in developing the size of our artillery, and it was found necessary to pass from grains of powder to pellets or pebbles and prisms of powder — that is to say, we converted powder into masses which burned, comparatively speaking, very slowly when ignited in the air, but which, when ignited in charges of 80 to 120 lbs., still burned very rapidly in the gun, and produced occasionally an unduly violent action, which it was desirable to moderate. We are talking of building very much bigger guns than.
the 35-ton gun, which requires a charge of powder weighing 120 lbs., and we shall therefore want a much tamer powder for those guns. I am consequently pretty certain that, as far as big guns are concerned, gun cotton has no future.

To carry out a complete comparison, one would have to factor in analyses of the other systems outlined above: the function of these incipient smokeless powders in military rifles and guns, the challenges of manufacturing guncotton (the safety problems were not completely solved in the 1870s), and above all, perhaps, the social and professional context of Abel's employment as War Office chemist. Abel was certainly not a completely free agent in his choice of research subjects (63).

III. Towards Smokeless Powder

In conclusion, I suggest that a set of analyses similar to the ones that have been put forth in the preceding parts of this paper could be extended to the revolutionary advent of smokeless powder in the 1880s and 1890s. The scheme can be followed with specific examples below.

The propellant system: guncotton to smokeless powders. Abel had succeeded in purifying and stabilizing guncotton by his method of pulping the material but had apparently ceased his research before he had achieved reliable control of its ballistic force in the military gun. This was accomplished by Paul Vieille by colloiding a mixture of guncotton and a less highly nitrated form of nitrocellulose in a suitable solvent under high pressure (64). This resulted in "plasticizing" the nitrocellulose and thus destroying completely its fibrous nature. Although Vieille was the first to succeed in producing a military smokeless powder, his success was not without precedent or context. The influence of two earlier developments on Vieille remains veiled: (1) various near colloidal powders produced as "sporting powders" in the early 1880s, about which a contemporary observer wrote, "The French military authorities took early note of their results (65)." (2) The invention of celluloid by the American, John Wesley Hyatt, in 1870, in his quest for a material from which to fashion the perfect billiard ball. Celluloid was a colloid of pyroxyline (collodion) achieved by subjecting a mixture of pyroxyline and camphor to heat and intense pressure (66). The American munitions chemist, Charles Munroe, implied a connection between the procedure for making celluloid and Vieille's for producing smokeless powder, which has recently been reiterated by Norman (67). (3) Finally, there was Alfred Nobel's invention of gelatinized nitroglycerine blasting explosive in 1875; this soon led Nobel to explore "double" smokeless powders (nitroglycerine/nitrocellulose base), resulting in the invention of "ballistite" shortly after Vieille's breakthrough.

The propellant-gun-projectile system: shotguns to military weapons. As already implied, in the 1870s and 1880s, there existed a market for guncotton where its characteristic of smokelessness was most attractive: as a propellant for sportsmen. In addition to Schultzze's powder, about thirty other compositions of pulped guncotton with oxidizing agents such as potassium or barium nitrate, or combustible diluents and binding agents sugar, cellulose, charcoal or sulfur, and gums, resins or paraffin, appeared on the commercial market. None was reliable enough for military use but served the sportsmen well enough to be commercially successful (68). A good technological analogy to the role of smokeless sporting powders of the 1870s and early 1880s is that of the transistor between its invention and the development of the microchip. In this interim, the transistor found a multitude of commercial uses in radio, hearing aids, etc.

By the 1880s, a demand for a smokeless powder was developing in the military with the appearance of powerful breech-loading, rapid-firing rifles, and machine guns. Also, the caliber of military small arms was growing smaller as the projectiles became lighter and more elongated for more precise trajectories, necessitating a more powerful propellant than gunpowder. Thus, the advantages of a powerful, nonfouling, smokeless powder became insistent (69). Already in France, smokeless powders based on picric acid had been developed, one of which (Brugère's powder) gave good results in the Chassepôt rifle and continued to be tested until it was superseded by Vieille's Poudre B (70).

The system of the scientific investigators: research style of Paul Vieille. As mentioned earlier, Paul Vieille (1854-1834) was a graduate of the École polytechnique. He then joined the corps of engineers of the gunpowder service, where he worked closely at the Dépôt (later Laboratoire) central des Poudres et Salpètres with Émile Sarrau, another polytechnicien, and with the chemist, Marcellin Berthelot, who had assumed a leading role in munitions research and organization after the Franco-Prussian War (71). Rice has characterized Vieille as an "engineer and explosives expert" in contrast to academic chemists like Mendeleev. He sees this contrast expressed in the type of smokeless powder each developed: Vieille was willing to use chemically inhomogeneous explosive mixtures, whereas Mendeleev searched for chemical homogeneity (72). I shall conclude by expanding a bit
on Rice's perceptive observation. I would argue that Vieille's research, often carried out in tandem with Sarrau, represented the coming together of virtually all of the research traditions of military munitions described above. It was the culmination of the French physicalist tradition of the polytechnicien military engineers. But it also built on the research of Rodman and of Noble and Abel, as well as the thermochemical tradition of Bunsen and Schischkoff, and of Berthelot.

This synthesis of research methodology was exemplified by Vieille's invention of the "bomb calorimeter" (bombe calorimétrique) in 1878. Essentially a refinement of Noble's "explosive apparatus (73)," it was employed by Vieille in the early 1880s to study systematically the explosions not only of black powder but also of guncotton. Critical to these studies was another refinement made by Vieille: to the crusher gauge, which he used to measure explosion pressure, he attached a recording device that could indicate pressure change throughout the course of the explosion (74). At this very time, Vieille was carrying out comprehensive studies of the chemistry of nitrocellulose and what proved to be the classic study of the manner in which explosives of all types actually burned (75).

Although the exact route Vieille took to the development of smokeless powder remains shrouded in mystery, it is likely that all of these investigations played their part in leading him to Poudre B. To illustrate this, I shall end by quoting from the most recent of the very few studies devoted to the background of this critical invention (76):

These experiments [with the bomb calorimeter] displayed correlation between the development of pressure of a given explosion and two characteristics of that substance: its compactness and its geometrical shape. Vieille thus saw why guncotton and other nitrocelluloses which normally have a fibrous structure exploded in a closed vessel with such an extreme rapidity as to render impossible use in a military gun. He conceived that guncotton would be susceptible to burn at a moderate speed after having been put into a sufficiently compact form. This is what he did in "gelatinizing" it by means of a volatile dissolvant, which could afterwards be eliminated. The material, in the form of thin plates, had a speed of combustion that could be regulated by modifying their [the plates'] thickness.

REFERENCES AND NOTES

7. C. C. Gillispie, Science and Polity in France at the End of the Old Regime, Princeton University Press, Princeton, NJ, 1980, Ch. 1.6, 50-73. I would hazard a suggestion for a reason for this inhibition of scholarship on modern munitions. It has to do with the paradigm that has dominated discussion of early modern military history: that of the "military revolution." Although military historians have disagreed intensely about what this "revolution" was (or, indeed, whether it was a single revolution), there has been agreement over the general point that, although the introduction of firearms was central to the early modern military transformation, their development had largely run its course by the end of the seventeenth century and was not to undergo major change until the second half of the nineteenth century. Hence, munitions must also have been a static (and historically uninteresting) technology in this period. This overlooks, among other things, the development of the role of science and science-related technology in the production and improvement of munitions.
10. "Gunpowder Section," International Committee for the History of Technology. Twenty one papers were presented at this section at the 1996 ICOHTEC meeting in Budapest.


13. The highly explosive guncotton, unlike collodion and other less highly nitrated forms, is insoluble in alcohol and ether.


16. Ref. 15, Footnote 1.


20. Ref. 7.

21. Ref. 9, pp 54-57.


23. For Gay-Lussac’s activities, see M. Crosland, Gay-Lussac: Scientist and bourgeois, Cambridge University Press, Cambridge, 1978, 181-187. He was involved in research concerning a number of different aspects of powder: refinement of saltpeter, analysis of powder composition, study of fulminates (with Liebig). He was also instrumental in getting the ballistic pendulum into use in France, as well as in the chemistry of the cannon.


27. O. F. G. Hogg, The Royal Arsenal: Its Background, Origin, and Subsequent History, Oxford University Press, London, 1963, Vol. 2, 749. There apparently had been a position of “ordnance chemist and assayist of metals,” which, however had been abolished in 1825; the last incumbent (of some twenty years), a Dr. McCulloch, was pensioned off. (Hogg, ibid., Vol. 1, 661.


29. West, Ref. 11: W. D. Cocroft, “William Congreve (1743-1814), Experimenter and Manufacturer.” ICOHTEC Conference, Budapest, 1996 (unpublished ‘speaker’s text’), p 2. Faversham Mills (Kent) were acquired in 1759; Waltham Abbey Mills (Essex) in 1787.

30. One result was the adoption of a new means of preparing charcoal in sealed retorts, apparently suggested by the chemist/cleric Richard Watson.


32. Col. R. Delafiel, Report on the Art of War in Europe in 1854, 1855, and 1856, George W. Bowman, Printer, Washington, DC, 1861, 5, 9. Delafiel was a member of an official military commission sent by the Secretary of War.


35. The minutes of the Ordnance Select Committee (1860-1869), the reports of this committee (1863-1869) and the reports of the Committee on Gunpowder and Explosive Substances are to be found at the Royal Artillery Library, Old Royal Military Academy, Woolwich Arsenal. The Committee on Explosive Substances issued its final report in 1880. There was also another committee on guncotton in the early 1870s.


40. In fact, after an explosion destroyed the magazine at Simmering, the opponents of gun-cotton won the day and the Austrians reverted to gunpowder. Norman, Ref. 12, pp 56-57. They continued to use it in shells.

41. Ref. 37, pp 6-7.


44. Theoretically, 100 parts by weight of pure cellulose ought to increase 83.3% in conversion to trinitrocellulose (C_6H_3N_3O_8). In studying Von Lenk’s process, Pelouze and Maury had found a maximum increase in weight of only 77.8% and had assigned a formula indicating a lower level of nitration (C_6H_3N_3O_8, 5N_2O_5). Abel had found an increase of weight ranging between 81.8 and 82.6%. Abel, Ref. 36, pp 306-308.

45. Ref. 42, p 208.


47. Abel mentioned that the pulping procedure had been developed in connection with experiments on substituting guncotton for gunpowder as a military propellant; Ref. 42, p 219.


50. This had been developed by the powder makers at Stowmarket [Messrs. Prentice] for cartridges for sporting guns. Abel did not yet have in mind Alfred Nobel’s development of dynamite; Ref. 49, pp 625-626.

51. Ref. 49, p 626.


53. Ref. 52, p 18. A contemporary artillery officer summarized the problems as follows: “A course of experiments carried on in 1865, at Woolwich, soon sufficed to show that gun-cotton, as then manufactured, was not suitable for artillery purposes. The great local violence of its action, and rapidity of its ignition when confined, as in the chamber of a gun, rendered it extremely destructive to the piece. Experiments were made with a view to diminish the destructive energy of the gases generated on the combustion of the cotton, but so far as they were carried out, it appeared that in reducing its explosive force, and diminishing these destructive effects, its power as a propelling agent was similarly reduced, and it was for the time decided to give up the idea of employing it for artillery. It has, however, still many supporters as an explosive for sporting purposes, though I am not aware that when made of such strength as to cease to be injurious to the gun, any great superiority over gunpowder, as regards hard hitting, is proved for it, though undoubted benefits arise from its freedom from smoke and fouling.” Col. A. a’Court Fisher, “Gun-Cotton Applied to Demolitions,” [Lecture: June 10, 1870], J. Roy. United Service Inst., 1871, 14, 419-447 (421).

54. Ref. 52, pp 518-519. The rifles were Enfield and Snider. At just this time, tests were underway to convert muzzle-loaders to breech-loaders: see P. Labbett, British Small Arms Ammunition, 1864-1938, P. Labbett, London, 1993, Ch. 1-2.

55. Ref. 52, pp 518-519.

56. George, Ref. 12, p 163; Norman, Ref. 12, p 79.

57. F. A. Abel, On Recent Investigations & Applications of Explosive Agents (BAAS Lecture, August, 1871), Edmonston and Douglas, Edinburgh, 1871, 20. Schupphaus, in his excellent article on the evolution of smokeless powder, wrote that Abel “experimented at Woolwich [1867-68] with cartridges built up from compressed gun-cotton fired from bronze field-guns, but found little encouragement, though the results were ahead of those obtained with Von Lenk’s cartridges,” “The Evolution of Smokeless Powder,” J. Mil. Serv. Inst. US, 1896, 18, 173.


The heaviest ordnance used in the Crimean War was cited as the context for the origin of this investigative program. Regarding the introduction of large grained gunpowder for heavy ordnance, Abel wrote: "This was the first very large powder which was introduced in England for heavy guns, but a very large grained powder had just previously been introduced in America, under the name of mammoth powder, and a much larger powder, of prismatic shape, also of American origin, was adopted about the same time in Russia and Prussia." (p 123). At the end of the talk, Abel discussed other measures taken to design the powder cartridge to avoid "wave-pressure" and to fit "gas checks" on the base of the projectile to control the otherwise destructive force of the charges in very large guns. (pp 124-127)

In an 1871 address by Noble, he credited Rodman as being "the first person who experimented on the effect of size of grain, and proposed prismatic powder" and wrote that Bunsen and Schischkoff's experiments "may justly rank among the most important which have been made on our subject." Noble, Ref. 58, pp 58, 63, respectively.

60. Noble and Abel, Ref. 58, Part I, pp 204-205.

61. Major-General Sir C. Callwell and Major-General Sir J. Headlam, The History of the Royal Artillery, Royal Artillery Institution, Woolwich, 1931-1940, Vol. 1, 172-173. They went on to say that, "The discoveries made in respect to the propellant, coupled with additional experience gained in relation to ballistics in general, may in fact be said to have brought about a revolution in the accepted principles of gun construction, as they were understood in this country."

62. F.A. Abel, "Gun Cotton." [A Lecture Delivered in the Hulme Town Hall, Manchester, on Wednesday, November 19th, 1873], Science Lectures for the People: Fifth Series of Science Lectures delivered in Manchester, 1873, John Heywood, Manchester, 1874, 69.

63. Abel had not abandoned hope for developing a guncotton propellant for use in military rifle and, as late as the mid-1870s, was still pleading for further research: Progress Report of the Committee on Explosives Substances, with Appendices. 1st April 1876, Her Majesty's Stationery Office, London, 1877, 74-75.

64. Insoluble nitrocellulose: 68.2 %; soluble nitrocellulose, 29.8 %; paraffin: 2.0 %, gelatinized in acetic ether. A. Marshall, Explosives, I. & A. Churchill, London, 1917, 1932, 2d ed., Vol. 1, 294. This was the result of an external analysis since the process and recipe were a military secret, perhaps the first such in the history of modern munitions.


68. Munroe, Ref. 67, pp 826-829; see also Worden, Ref. 14, Vol. 2, Ch. 18.

69. Munroe, Ref. 67, pp 823-824; see also Schupphaus, Ref. 57, p 174. The ascendancy of new types of gunnery like the machine gun directly impelled the British military authorities to renew the search for a smokeless powder in 1886 and to involve Abel in this search. See the dossier at the Public Record Office: SUPP 5 568, "Experimental Powder from April 1885-17-7-91." In one letter, Abel berated the Superintendent of the Royal Gunpowder Factory, Waltham Abbey, for not allowing him to use the testing facilities there: "I regret that you do not see your way to continue to afford facilities for the working out of the experiments made with a view to ascertain whether a smokeless powder for machine guns is attainable, a subject which was referred to us jointly to investigate." Abel to Superintendent, Royal Gunpowder Factory [W. H. Noble], August 17, 1887.

70. Schupphaus, Ref. 57, pp 173-174; according to Guttmann, Ref. 19, Vol. 2, p 237, Vieille's original smokeless powder was made of both picric acid and guncotton.


72. Rice, Ref. 46, pp 9-11. He linked Abel to Vieille in this regard.

73. I have not yet found evidence of a direct affiliation between the two.

74. The relationship between Noble's crusher gauge and the instruments used by the French was spelled out by Paul F. Chalon: "Le crusher, ou écraseur, de la commission d'constitution des charges de fusil long, a été perfectionné par M. Berthelot, et il est actuellement employé par la commission des matières explosives et dans les expériences exécutées par l'artillerie de marine, en France." Tracté théorique et pratique des explosifs modernes et dictionnaire des poudres et explosifs, E. Bernard et Cie, Paris, 1889, 2d ed., 191-192.

75. P. Vieille, "Étude sur le mode de combustion des matières explosives. mémorial des poudres et explosives, 1893, 6, 256-391.

76. Ref. 70, p 402; see also L. Médard, "Paul Vieille et son oeuvre," Mémorial de l'artillerie française, 1986, 60, n° 2, 11-23.
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SAMPLING PARSONS MULLIKEN: PIONEER IN ORGANIC QUALITATIVE ANALYSIS

David L. Adams, University of Massachusetts, Amherst

Introduction

Most chemistry majors in the decades from the 1910s through the 1970s remember the organic qualitative analysis laboratory—some fondly, some otherwise. Whatever the recollection, “organic qual” served and continues to serve many purposes, most notably the development of critical thinking and logical analysis skills. Systematic organic qualitative analysis as a means to teach organic chemistry was largely an American invention, begun in the late nineteenth century by Dr. Samuel Parsons Mulliken at the Massachusetts Institute of Technology (MIT) (1, 2). Mulliken spent most of his career researching, teaching, and writing books about organic qual at MIT. This paper details the pioneering role of Professor Mulliken in the development of systematic organic qualitative analysis and presents some related aspects of his academic life. An earlier publication in THE NUCLEUS, the official publication of the Northeastern Section of the American Chemical Society, although touching on the development of organic qual, was mainly devoted to Mulliken’s personal life and professional career (3).

Early Life in Newburyport, Massachusetts

Sam Mulliken was born in the family home at 46 High Street in Newburyport on December 19, 1864. His early interest in chemistry grew from reading “Conversations on Chemistry” by Jane Marcet, the same book that both his father, Moses Mulliken, and his son, Robert (chemistry Nobel Prize, 1966), read (4, 5). After graduating from Newburyport High School in 1881, Sam worked for two years in a local apothecary shop. With the help of one of the first Wheelwright Scientific Fund scholarships (6), he entered MIT in the fall of 1883. Sam’s long-time friend and fellow Newburyport native, Arthur Amos Noyes, also entered MIT that same fall. Like Mulliken, Noyes received a Wheelwright scholarship and studied chemistry. As youngsters, Noyes and Mulliken performed chemical experiments together at both their family homes, sometimes to the dismay of their parents (4).

Graduate School

After graduating in chemistry from MIT in 1887, Sam taught chemistry at the University of Cincinnati for one year as an Assistant in Chemistry. He, together with fellow MIT graduates Arthur A. Noyes (‘86), Augustus H. Gill (‘86), and Frederick F. Bullard (‘87), then traveled to Germany to pursue graduate study. Although he originally intended to work in Adolf von Baeyer’s lab in Munich, Sam eventually enrolled at the University of Leipzig to work under the direction of Johannes Wislicenus. Mulliken received his Dr. in chemistry in the summer of 1890 and returned to America (7, 8).

Sam spent the winter of 1890 conducting physical-chemical research at MIT. In spring 1891 he obtained a position as Fellow in Chemistry at the newly established Clark University in Worcester, Massachusetts (9). During the 1891-92 academic year he worked at Bryn Mawr College as Associate in Chemistry, then returned to Clark to work as both Instructor in Organic Chemistry and
Acting Head of the Chemistry Department from 1892-94. While at Clark he conducted and directed research on the electrolysis of organic compounds (10). Subsequently, he worked for a year as a Research Assistant in Oliver Wolcott Gibbs' private laboratory in Newport, Rhode Island. In the Fall of 1895 Sam accepted an appointment as Instructor in the Chemistry Department at MIT (11, 12). While at MIT he was promoted to Assistant Professor in 1905, Associate Professor in 1913, and Professor in 1926 (13).

Massachusetts Institute of Technology - The Early Years and Arthur A. Noyes

Arthur A. Noyes had been in the MIT chemistry department for five years when Mulliken returned as a faculty member in 1895. Noyes, though initially trained as an organic chemist, soon embraced physical chemistry while simultaneously developing a life-long interest in inorganic qualitative analysis. As early as 1892 Noyes published a set of notes for the inorganic qual class at MIT (14). He wrote these because the available texts were either too brief or too encyclopedic for the undergraduate laboratory (15). In the preface to the third edition of the notes, written in 1897, he stated (16):

...qualitative analysis is a satisfactory method of teaching a part of descriptive chemistry chiefly because it unites into a connected whole a great variety of isolated facts, and because it makes evident to the student a practical use of the information presented to him.

In further pursuance of this dual “descriptive chemistry” and “practical use” approach, Noyes and the newly appointed Sam Mulliken set out at once to revamp the organic laboratory (17). As a result of their work, the descriptions of the organic laboratory changed, reflecting the shift in pedagogical philosophy. In the 1896-97 MIT catalog the organic laboratory is described as including (18):

...comprises practice in the methods of ultimate analysis, exercises in the preparation of a variety of typical organic substances, and a series of experiments illustrating the characteristic reactions of the different classes of substances and their identification and separation (emphasis added by author).

The “series of experiments” highlighted the descriptive chemistry of the organic functional groups and the “identification and separation” illustrated a practical use of this knowledge. Thus the emphasis on descriptive chemistry and practical use initiated in the inorganic qual course was applied to the organic laboratory course. The 1896-97 MIT Annual Report states (20):

......the special course of laboratory experiments on the detection and separation of the various classes of organic compounds, inaugurated last year...has been considerably extended and improved by the publication of a textbook to accompany it. So far as is known, a course of this kind is not as yet presented by any other institution. The success which has attended its introduction here, is, therefore, worthy of special notice.

Organic qualitative analysis as a part of the chemistry curriculum was born

The exact date on which these changes came into effect is difficult to determine because the inclusion of events in official catalogs and reports often follows their actual implementation. However, the facts that the accompanying textbook was published in 1896 (21), and that the 1896-7 annual report contains a discussion of the altered course suggest that the change was made in the fall of 1896. The fact that a description of the revised laboratory program first appeared in the 1897-8 catalog is explained by the early publication date of the catalog. It is reasonable to conclude that Mulliken and Noyes began their collaboration on organic qual as soon as Mulliken arrived in the fall of 1895, if not before.

The First Textbook

Laboratory Experiments on the Class Reactions and Identification of Organic Substances, pub-
lished in 1896 by Noyes and Mulliken (21), was the first systematic treatment of organic qualitative analysis designed for the academic laboratory. In the preface to its 1915 third edition it is stated that this is a (22):

......supplement to the ordinary course of instruction in preparation work (and)......although the primary purpose of the experiments ... is to illustrate the characteristic reactions of organic compounds, their analytical significance is a feature of no slight importance ....

The descriptive and practical aspects of this work were distinctly different from the usual routine organic synthetic methods of the time. Notably, Ira Remsen commended the text, stating that some books drive one “to get into a rut, to work mechanically ... without any accompanying action of the mind” and some do not. He counted the Noyes and Mulliken text in the latter category and suggested that it “will be of service” (23).

This was Mulliken’s first, brief foray into a succession of treatises spanning the next 26 years, in which he outlined the analysis and identification of pure organic compounds. His interest in organic compound identification eventually turned his entire professional activities toward this effort. He developed and taught courses in undergraduate and graduate organic qualitative analysis; his thesis students worked on applicable laboratory techniques; and he limited his writing and speaking activities to the organic qualitative analysis volumes he was researching and about to publish.

The Mulliken Scheme for the Identification of Pure Organic Compounds

In the late 1890s Mulliken’s research efforts shifted completely to his organic qual work. His conference presentations and publications included papers on the detection of methyl alcohol alone (24), and in mixtures (25) and the detection of the nitro group (26). After about 1900 he appears to have abandoned publishing separate journal articles on analysis and class reactions, opting instead to publish them as part of a major work on systematic organic qualitative analysis.

In February of 1903, at a meeting of the Northeastern Section of the American Chemical Society, Mulliken outlined his organic qualitative analysis scheme in an address entitled “How May an Unknown Organic Compound Best be Identified?” He is quoted in the notes of the meeting as claiming that (27):

......any organic compound may be accurately identified in much less time than by determining its composition by combustion, etc.

In 1904, after eight years of painstakingly detailed laboratory work, Mulliken published A Method for the Identification of Pure Organic Compounds - Volume I (28). This volume contains a detailed description of a method for the systematic identification of organic compounds containing carbon and hydrogen or carbon, hydrogen, and oxygen. It also includes descriptions of about 2,300 pure organic compounds composed of these elements. The method is based largely on chemical reactions, although some tests for physical properties are included. Subsequent Mulliken “Methods” volumes followed: Volume III (29) in 1910 deals with commercial dyestuffs; Volume II (30) in 1916 contains a description of organic compounds containing nitrogen; and Volume IV (31) in 1922 is a compilation of organic compounds containing elements other than carbon, hydrogen, oxygen, and nitrogen. The classification scheme, later known as the “Mulliken Scheme,” developed in these “Methods” books was the first comprehensive, systematic approach to identify organic compounds by chemical reactions and physical properties. The “Methods” books were renowned for their extensive compilations of properties.
of organic compounds, the thoroughness with which all the qualitative schemes were described and tested, and the care taken to describe precisely the results (32).

The Mulliken qualitative analysis scheme is based on the use of chemical reactions and physical properties to categorize unknown organic compounds into orders, suborders, genera, and divisions. It provides additional identification tests to confirm a specific compound or species. Mulliken compared his qualitative analysis classification with Carolus Linnaeus' classification scheme developed for living things. He said his scheme was (33):

...designed to secure for the carbon compounds those advantages which have been already so long enjoyed in Botany and other branches of Natural History through the use of systematized descriptions of salient characteristics.

It is not surprising therefore, that Mulliken grouped organic compounds into orders, suborders, genera, divisions, and species.

In Mulliken's organic qualitative scheme, organic compounds are grouped into orders based on their elemental composition, and into genera based on chemical reaction tests. The species or chemical substances within each genus are arranged by some readily determined physical constant such as boiling or melting point. The genera are subdivided into divisions that represent solids or liquids. The scheme begins with a series of ordinal tests applied in hierarchical fashion, to determine the order of the species. Volume I deals only with Order I—that is, C, H or C, H, O—compounds. Volume II deals with Order II compounds, containing C, H, N, O. Volume IV deals with Orders III, IV, V and VII compounds containing chlorine, bromine, iodine and sulfur, respectively, in addition to C, H, and O, and several of the "higher orders" which contain various combinations of additional elements. For example, Order L contains chlorine and nitrogen in addition to C, H, and O. Volume III, which deals with commercial dyes, was not an integral part of the Mulliken qualitative analysis scheme.

Once its order is established, a compound is then placed into a genus by conducting a series of prioritized tests in sequence. For instance, for an Order I compound, the nine generic tests distinguish among aldehydes, carbohydrates, acids, phenols, esters, anhydrides, ketones, alcohols, and hydrocarbons. After the order and genus are determined, the boiling or melting point of the species is compared with those of known species listed in the same order and genus contained in the extensive lists provided in the book. Finally, examination of physical properties and confirmation tests establish compound identity (34).

Prior to the publication of the Mulliken Scheme in 1904 the only method for identification of previously characterized organic compounds was by empirical formula determination from combustion analysis, a lengthy and sensitive process. Mulliken considered his scheme more useful to practicing chemists because it did not rely on combustion analysis, was accurately conducted in any organic laboratory, and consumed less time than available methods (35).

The subject matter of the theses written by his undergraduate students shows the evolution of Mulliken's analysis scheme. Beginning in 1897, his students explored the usefulness of reagents such as sodium, sulfuric acid (36), and acetyl chloride (37) in classifying organic compounds. It would appear that, during this time, he and his students experimented in determining suitable reagents to distinguish among major groups, or what were later called orders and genera, of organic compounds. Later student research became somewhat more focused on dealing with identification of specific compounds or species within genera. For example, Rickards' work in developing a method for the identification of the more important carbohydrates and glucosides (38) resulted in a complete scheme for the individual identification of many carbohydrates. This scheme provided much of the framework for the identification of Order I, Genus II compounds—the carbohydrates. Sam's undergraduate students are acknowledged by name in the prefaces to Volumes I and II of the Methods series. The use of undergraduates in this research was essential because MIT awarded very few masters and no doctorates during the time Mulliken was actively pursuing the details of the scheme.

Other Organic Qual Schemes

Shortly after Mulliken's pioneering publication appeared in 1904, others put forth their own organic qualitative analysis schemes. One of the most successful was that taught in 1920 by Oliver Kamm at the University of Illinois (39). He based his scheme on the solubility classification of organic compounds into seven groups, and subsequent identification by physical and chemical properties and derivative preparation. Kamm published his scheme in 1922 in a book entitled Qualitative Organic Analysis - An Elementary Course in The Identification of Organic Compounds (39). In the preface to the book he states that(40):
The chemist to whom most credit is due for the development of organic qualitative analysis is Professor S. P. Mulliken.

In the same preface he refers to Mulliken as “the pioneer in the field.” Indeed, Mulliken was the pioneer in the field but it was Kamm’s solubility approach that quickly emerged as the organic qual scheme used in colleges and universities around the country. In the preface to the second edition of his book, Kamm mentions over twenty organic chemistry teachers from around the country who used his first edition, and who provided suggestions for the second (41). On the contrary, Mulliken’s “Methods” books, although frequently used as references (42), were rarely assigned as laboratory texts.

In 1935 Ralph Shriner and Reynold Fuson, both from the University of Illinois, published their text, The Systematic Identification of Organic Compounds - A Laboratory Manual, which was based on Kamm’s original solubility scheme (43). Shriner and Fuson’s seventh edition (with co-authors) is still used in some colleges today. However, the increased availability and usefulness of spectroscopic methods beginning in the late 1960’s resulted in the end of the organic qual course, as it was known in the first half of the century.

In 1929 Mulliken invited his MIT chemistry department colleague, Ernest H. Huntress, to work with him in both revising the “Methods” books and condensing their analytical procedures into a manual suitable for use in the undergraduate laboratory. Huntress partially accomplished the first of these tasks by revising Mulliken’s Volume I, which was published in 1941 (44). Huntress worked essentially alone in this effort because of Mulliken’s death in 1934. Volumes II and III were never revised. Huntress did, however, update Volume IV during World War II because of the growth in the number of higher order compounds and the specific interest of the Chemical Warfare Service in Order III chlorine-containing compounds (45). This new volume, entitled Organic Chlorine Compounds, was published in 1948 (46). During the 1930s Huntress also produced and locally published a laboratory manual based on the "Mulliken-Huntress” scheme for use by MIT students (47). Although intended for MIT students, the Mulliken-Huntress lab manual was used by many other colleges (48). In the early 1950s Huntress passed on the rights to the scheme to Dr. Edward R. Atkinson, his former doctoral student (Ph.D. 1936) and Mulliken’s former lab assistant in 1933 (45). Dr. Atkinson retains these rights to this day, although he has not revised or republished the scheme.

In the final analysis it appears that the reasons the Mulliken, later the Mulliken-Huntress organic qual scheme never gained wide popularity were many. The original “Methods” books were not intended for undergraduate laboratory instructional use, but rather for professional analysts and as reference works (49). Contemporary texts used in the undergraduate laboratory, for instance, Clarke’s Handbook of Organic Analysis, were comprehensive, single volumes containing tables of only the most common organic compounds (50). By the time Huntress condensed the “Methods” texts into a practical, single volume manual of procedures, the Shriner and Fuson text was widely available. Further, the Huntress-Mulliken manual was published locally and primarily known by word of mouth (45, 51). It contains neither discussion of mixture separation nor student problems, unlike the Shriner and Fuson text, which was marketed nationally. Furthermore, the latter text relied more extensively on derivative preparation than on the extensive compilation of information about individual organic compounds found in the Mulliken-Huntress manual. For all these reasons, the popularity of the Shriner and Fuson text rose and that of Mulliken-Huntress faded. Later editions of the Shriner and Fuson text are in use today while the Mulliken “Methods” texts and the Mulliken-Huntress manual are rarely found.

Dye Chemistry

Mulliken had a life-long interest in dye chemistry and consulted in the dye industry. This interest likely developed because of the timely importance of the textile industry in his Newburyport home town, the applied
nature of chemistry taught at MIT, and the fact that many MIT students were employed in the textile industries. The nearby cities of Lowell and Lawrence were renowned for their textile mills, and Lowell was home to the Lowell Textile Institute and the famous textile dye authority, Louis Olney. Sam developed and taught a course in dye chemistry at MIT, and he regularly took students on field trips to textile companies in Lawrence as part of the course. His long-standing interest in dyes is evidenced in “Methods” Volume III that deals with the qualitative analysis of commercial dyestuffs. Mulliken had no intention of writing a separate volume on the identification of commercial dyestuffs but was apparently persuaded that this venture was of sufficient importance to put aside his work on completing Volume II. Indeed, Volume III appeared six years before Volume II! An explanation as to why the dyestuffs volume was pursued and completed prior to Volume II is open to speculation. Mulliken may have been pressured by outside sources to help the American textile industry in the identification of commercial dyestuffs or it may have been that Mulliken intended to include the dyestuffs as part of Volume II but determined that they would be more effectively treated separately. Potential arguments for both these scenarios are to be found in Chapter One of Methods – Volume III.

The Later Years

During his 39 years of teaching at MIT, Mulliken taught courses in undergraduate organic chemistry, qualitative organic analysis, chemistry of dyes and dyestuffs, and heterocyclic chemistry. Outside the classroom Sam was active in the professional chemistry society Alpha Chi Sigma, served on several MIT committees such as the Committee on Determining Official MIT Colors, and represented his graduating class of 1887 at Alumni Council meetings. He also occasionally accepted administrative responsibilities. One such position was as Head of MIT’s Undergraduate Organic Chemistry Division from 1925 to 1934, when he directed the undergraduate instructional work (53,54). In 1933, Sam was asked to pass judgment on an MIT undergraduate who sought a waiver from the organic chemistry requirement. Reluctant to grant such a waiver, believing that the requirement should be fulfilled, he met with the student and eventually allowed him to take the course final examination. The student passed and Sam approved the waiver (55). The student was Robert Burns Woodward, and no one would deny that Mulliken’s decision in this case was indeed warranted!

By the Spring of 1934 Sam was old and tired, regularly falling asleep in his Morris chair in his office in Room 4-440 at MIT. He last taught during the 1933-34 academic year and then took his second leave of absence from MIT for the fall of 1934. During his first leave in the fall of 1918 he had worked for Chemical Warfare Service. In the summer of 1934 he contracted rheumatic fever and was hospitalized in Newburyport. He died at home of a coronary thrombosis on October 24, 1934 and was buried at the Oak Hill Cemetery in Newburyport. Many MIT chemistry department faculty attended the funeral. Ten MIT faculty served as pallbearers: Frederick G. Keyes, Augustus H. Gill, James F. Norris, Arthur A. Blanchard, Avery A. Ashdown, Tenney L. Davis, Avery A. Morton, Ernest H. Huntress, N. A. Milas, and Robert T. Armstrong (56,57). Sam’s tombstone is engraved with his professional achievements, including his Dr. from Leipzig and posts he held at MIT.
Upon his death in 1934, Mulliken's professional belongings in Room 4-440 at MIT passed on to his faculty colleague and organic qualitative analysis collaborator Ernest H. Huntress. Over the next several years Huntress gradually disposed of the voluminous chemical samples Sam had stored there. Today, after renovations at MIT, no trace of Mulliken's office and laboratory space remains. There is, however, a photograph, circa 1899-1900, of the MIT Chemistry Department in a lobby on the first floor of Building 4 honoring Ellen Swallow Richards. Samuel Parsons Mulliken is in the second row, third from the right, directly behind Mrs. Richards (58).

NOTE: A complete listing of the publications of Samuel Parsons Mulliken and a listing of his known students and their thesis titles are available from the author upon request.

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### ABOUT THE AUTHOR

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### BSHS IVAN SLADE PRIZE

The British Society for the History of Science is pleased to announce the inauguration of a new prize generously donated by one of its members, Dr. Ivan Slade. The competition will take place biennially, and the prize of GBP 300 is offered for an essay (published or unpublished) that makes a critical contribution to the history of science. Examples would be scholarly work that critically engages a prevalent interpretation of a historical episode, scientific innovation, or scientific controversy.

The prize will be awarded for the first time in 1999. Submissions are now invited. There is no age limit, and entry is not limited to members of BSHS or UK citizens. Entries should be in English and should have been published or written in the two years prior to the closing date. They should not exceed 10,000 words in length and should be accompanied by an abstract of 500 words. Three copies of the essay and abstract should be sent to the BSHS Secretary, Dr. Jeff Hughes, CHSTM, Maths Tower, University of Manchester, Manchester. M13 9PL, to arrive by October 31, 1999.
J. A. R. NEWLANDS' CLASSIFICATION OF THE ELEMENTS: PERIODICITY, BUT NO SYSTEM (1)

Carmen J. Giunta, Le Moyne College

Introduction and Definitions

It seems safe to say that a place in the history of chemistry is assured for J. A. R. Newlands, yet even a century after his death debate continues over just what that place should be (2). Newlands was one of several scientists who published a system for classification of the chemical elements or explored the relationship between atomic weights and chemical properties in the decade following the 1860 Karlsruhe Congress. By the end of that decade the periodic system of the elements had emerged, and the question of priority for that system has engaged both chemists and historians of chemistry ever since. Opinions concerning the amount of credit which Newlands deserves for uncovering the periodic law varied greatly during his lifetime and still continue to do so.

The purpose of this paper is not to argue the relative merits of the contributions of Alexandre Émile Beguyer de Chancourtois, Dmitrii Mendeleev, Julius Lothar Meyer, Newlands, William Odling, and others. Rather, it is to examine the work of one scientist, Newlands, and ask whether that work constituted a periodic system of classifying the elements. The aim of this paper is not an attempt to reconstruct the process or sequence of events which Newlands followed to arrive at his views on chemical periodicity, but an attempt to examine his published views and appraise their validity from a contemporary point of view.

A brief summary of Newlands' life is appropriate before analysis of his work. (Details can be obtained from Newlands' obituary in Nature (3) and the entry on Newlands in the Dictionary of Scientific Biography (4).) John Alexander Reina Newlands was born on November 26, 1837. He spent most of his life in the vicinity of London, where he died on July 29, 1898. He studied at the Royal College of Chemistry and then served as assistant to the chief chemist of the Royal Agricultural Society. He spent part of 1860 on the European continent, but not at the Karlsruhe Congress, a gathering that has been described as necessary for the subsequent discovery of chemical periodicity (5). Instead, Newlands, who was of Italian descent on his mother's side, fought for Italian indepen-
dence with Garibaldi. In the mid-1860s Newlands published several notes in the Chemical News on relationships among equivalent weights, classification of elements, and a relationship he termed the "law of octaves." At the time, the work was the subject of little notice, some criticism, and even some ridicule. During this time, Newlands supported himself as a private analytical chemist and teacher. He later worked at a sugar refinery and concentrated on sugar chemistry, writing several articles and a book (6) on the subject, mainly in collaboration with his brother Benjamin. As the periodic law in the form proposed by Mendeleev and Meyer gained attention and acceptance in the 1870s and 1880s, Newlands began to assert his priority in the matter in articles in the Chemical News and in a monograph, On the Discovery of the Periodic Law and on Relations Among the Atomic Weights (7). He was awarded the Davy medal of the Royal Society in 1887 "for his discovery of the Periodic Law of the chemical elements," five years after Mendeleev and Meyer were given the same award for the same discovery.

It is necessary to define terms, and in particular to specify what is meant by a periodic system of the elements, before any analysis can be made. Unfortunately, the term periodic system does not have a universally accepted definition. The literature of the history of the periodic system is replete with definitions. Various contributors to the concept of chemical periodicity and historians of that concept even use different terms, including periodic law and periodic table. For example, Mendeleev used the term periodic law (8), a term which Newlands also embraced in asserting priority for his own contributions (7). J. W. van Spronsen, in his classic monograph (5), prefers the term periodic system. In discussing priority, van Spronsen defines a periodic system as, "a sequence of all the (known) elements arranged according to increasing atomic weight in which the elements with analogous properties are arranged in the same group or column." Earlier in the same work, however, van Spronsen refers to "facets of a true periodic system" including additional criteria, for example a distinction between main groups and sub-groups and provision of vacant spaces for undiscovered elements.

I propose a working definition that falls somewhere between van Spronsen's first definition and his true periodic system: a periodic system of the elements consists of a self-consistent arrangement by atomic weight of all the known elements, which systematically displays groups of analogous elements. This definition places considerable emphasis on organization and internal consistency. It does not, however, require the system to be free from error.

This study, in addition, applies to Newlands' work a set of secondary criteria enumerated by Sheldon Lachman for judging scientific theories. Lachman asserts that there are reasons for preferring one theory over another, even in cases where competing theories explain the data comparably well. His list of criteria includes clarity (explicitness and lack of ambiguity), completeness (in accounting for all known phenomena within its purview), coherence (internal consistency among its parts), simplicity (few independent assumptions or poorly defined concepts), fruitfulness (in advancing knowledge), and precision of prediction (9). Lachman's list is a clearly elucidated portion of an expository monograph that presents a traditional view of how science operates. His criteria, however, are representative of characteristics which a broad range of scientists and philosophers of science would expect in adequate scientific theories. Scholars who hold a traditional view of the practice of science (such as Lachman) as well as scholars skeptical of the traditional view (such as Thomas Kuhn) share similar criteria. Kuhn's list of standards for theory evaluation includes accuracy, consistency, scope, simplicity, and fruitfulness. "Together with others of much the same sort," he writes, "they provide the shared basis for theory choice (10)."

The Case for Newlands

Although Newlands' work does not meet the criteria for a periodic system set out above, his contributions were substantial. Those contributions extend beyond the tables most often reproduced in discussions of his work, and they include insights which have been misunderstood by critics both in his time and in ours. This section concentrates on Newlands' insights, deferring critical analysis of the shortcomings of his work.

Newlands is best known today for his law of octaves and the tables with which he illustrated that "law." Having arranged the elements in order of atomic weight and assigned an ordinal number to each element, he noticed the following relationship (11):

It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. ... This peculiar relationship I propose to provisionally term the 'Law of Octaves.'
Table I accompanied Newlands’ first formulation of the law of octaves in 1865. He presented a slightly improved version, shown in Table II, in a paper read before the Chemical Society in the following year (12).

The tables certainly constitute an arrangement by atomic weight of the elements then known. The arrangement shows elements with analogous properties in analogous positions. Newlands remarked (11):

It will be observed that elements belonging to the same group usually appear on the same horizontal line.

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<td>Li</td>
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<td>Al</td>
<td>11</td>
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<td>24</td>
<td>Ce &amp; La</td>
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<tr>
<td>C</td>
<td>5</td>
<td>Si</td>
<td>12</td>
<td>Ti</td>
<td>18</td>
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<td>N</td>
<td>6</td>
<td>P</td>
<td>13</td>
<td>Mn</td>
<td>20</td>
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<td>Di &amp; Mo</td>
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<tr>
<td>O</td>
<td>7</td>
<td>S</td>
<td>14</td>
<td>Fe</td>
<td>21</td>
<td>Se</td>
<td>28</td>
<td>Ro &amp; Ru</td>
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Notice that he did not claim that all elements which appear on the same horizontal line belong to the same group. Indeed, he gave as an example the nitrogen group, which he enumerated as containing nitrogen, phosphorus, arsenic, antimony, and bismuth, an example which lists as a group only some of the elements appearing on the same horizontal line. Newlands can certainly be criticized for not making his rows and groups co-extensive; however, to point to a row in his table and ask what the included elements have in common (as was done in a recent article on the development of the periodic law (13)) constitutes a misreading.

In 1863 and 1864, before formulating the law of octaves, Newlands made several predictions of elements not yet discovered (14, 15, 16). The most striking of these predictions was of an element of atomic weight 73 analogous to silicon, tin, and titanium (15). This element — germanium — was discovered in 1886 by Clemens Winkler. Newlands made this prediction in 1864, before Mendeleev (17), and he reasserted it in print at least twice after promulgating the law of octaves and before Winkler’s discovery (7, 18). The prediction of new elements is inconsistent with the law of octaves as Newlands formulated it, but it is important to note that Newlands did not abandon his earlier predictions after putting forward his "law." Newlands' predictions of new elements were based on incomplete triads of chemically similar elements whose atomic weights stood in an arithmetically simple relationship. Early in the 19th century, Johann Döbereiner had been the first to note such triads (complete ones) and to attempt to use them to group elements (19). Typically the atomic weight of
the triad’s middle element was the mean of those of the other two. In 1857, Dumas had examined relationships among atomic weights in groups of related elements (20). Newlands cited Dumas’ work, and his own early efforts at classification focused on groups of related elements and the relationship among their atomic weights.

Newlands’ prediction of germanium was better than others he made—even apart from the fact that it turned out to be correct. The prediction of germanium was based on more than one piece of evidence, more than one incomplete triad of related elements: namely, silicon, tin and silicon, titanium, ___ An individual triad was a somewhat flimsy basis for prediction, but two supported each other. In addition, the prediction of germanium concerned relatively light atoms which were better known at the time. If the list of elements can be compared to a jigsaw puzzle, it is certainly easier to predict and describe a piece missing from an area of the puzzle with relatively few gaps and whose patterns are fairly well known than to predict a piece missing from an area where gaps abound and possible patterns are little more than speculations.

Besides the prediction of germanium, which was borne out by subsequent events, Newlands and Mendeleev actually shared another prediction, this one incorrect. Both expected that an alkali metal of atomic weight near 170 would someday be found (15, 21). This and other incorrect predictions by Newlands were wrong for the same reason as this and another by Mendeleev, namely the existence of the mostly unknown lanthanide block between the second and third transition groups. The general superiority and specificity of Mendeleev’s predictions based on his periodic table are not in dispute. Newlands’ most successful prediction was not just a lucky guess, however, and his unsuccessful predictions were no worse than some of Mendeleev’s.

Newlands may be credited with speculating about the existence of whole families of undiscovered elements, a speculation borne out by the discovery of the noble gases in the 1890s. Faced with the criticism that his law of octaves left no room for the discovery of new elements, Newlands responded (22):

The fact that such a simple relation [the law of octaves] exists now, affords a strong presumptive proof that it will always continue to exist, even should hundreds of new elements be discovered. For, although the difference in the numbers of analogous elements might, in that case, be altered from 7, to a multiple of 7, of 8, 9, 10, 20, or any conceivable figure, the existence of a simple relation among the numbers of analogous elements would be none the less evident.

Of course, this statement is not a prediction of a family or families of new elements; furthermore, it does not address the usual course of subsequent discoveries of elements (i.e., not in families but as isolated members of already known groups). Still, the discovery of argon did present some difficulties with respect to the periodic system as it then existed because there appeared to be no place for it. Newlands’ speculation foresaw that such a discovery need not be problematic.

Newlands must also be credited with associating each element with an ordinal number. Indeed, Wendell Taylor’s assessment (23) of Newlands’ work called him a “pioneer in atomic numbers” and judged his emphasis on the ordinal number of each element to be “one of the most interesting features of his work.” For several reasons, that number is not the same as the atomic number known today. First, the discovery of elements unknown to Newlands would increase the order number he assigned to heavier elements. Also, he assigned the same number to elements whose atomic weights were very close; however, each element actually has a unique atomic number. Finally, Newlands was not aware of the physical basis for atomic number first elucidated by Moseley half a century later (24).

Newlands emphasized that atomic weight and order number were approximately proportional over large ranges of atomic weights. He considered his ordinal numbers as a regularly varying surrogate for the somewhat irregularly varying atomic weights. By focusing on order numbers rather than atomic weights, he could notice that an increment of 7 or 14 was frequently seen between similar elements—even if his tables included some inversions in order number. Newlands proposed the law of octaves, a relationship among order numbers, at virtually the same time as his first paper on this relationship between atomic weights and order numbers (25). He continued to explore the relationship between atomic weight and ordinal numbers well into the 1870s (26).

In fact, Newlands saw the ordering of the elements by atomic weight as one of the innovations for which he deserved credit; he asserted that one of his papers (15) in 1864 (7):

..gave a list of all the then known elements in the order of atomic weight, which was the first ever published.

The listing of elements by atomic weight is so common today that the claim sounds incredible. Even though it is not strictly correct (for example, John Hall Gladstone had published such an arrangement (27), albeit with
many erroneous atomic weights, in 1853; and even Dalton's incomplete list of unreliable weights was in numerical order (28)), the arrangement was sufficiently unusual even in 1875 that Newlands published a note extolling its advantages in data tabulations (29).

**Why Newlands’ Insights Do Not Constitute a Periodic System**

Newlands’ work on classification of the elements exhibited many of the features which are associated with the periodic system today and which won such acclaim for Mendeleev (e.g., recurrences of elements with similar properties, predictions of undiscovered elements). Mendeleev did not simply develop a better periodic system than Newlands; however; rather, Newlands’ work did not constitute a periodic system. This judgment hinges on the word system, with its implications of self-consistency and organization. In short, Newlands’ work on classification contains too many inconsistent or poorly defined pieces.

For example, the prediction of new elements, which was so prominent a feature of Mendeleev’s system, represents a contradiction in Newlands’ work. The law of octaves was criticized at the outset for leaving no room for the discovery of new elements (12). Although Newlands disputed this criticism, the fact remains that the law of octaves left no room for the prediction of new elements. His predictions of new elements, including the correct prediction of germanium, were all made before his formulation of the law of octaves, and they were made on the basis of relationships between atomic weights, not order numbers. Newlands’ contemporaries, presented with the law of octaves, might reasonably have assumed that he had abandoned his predictions for an arrangement he considered superior. Yet Newlands claimed priority in predicting germanium after Mendeleev’s prediction of gallium proved correct but before germanium was actually discovered—in effect reasserting the prediction.

The issue of just how or even whether the law of octaves was consistent with the discovery of new elements presents further instances of inconsistency or lack of clarity. That Newlands foresaw the possibility of new groups of elements has already been noted. His response to the far more common occurrence of the discovery of a new element or a re-evaluation of an atomic weight, however, reveals a logical difficulty (22):

As a proof, however, that new discoveries are not very likely to destroy such relationship, I may mention that when the existence of the “law of octaves” was first pointed out (Chemical News, August 20, 1864), the difference between the numbers of P and As was 13 instead of 14, as between As and Sb, and also between Sb and Bi. Since then, by the determination of the atomic weight of indium, the difference of the numbers of P and As has been made to be 14, as in the other cases adduced.

His argument here would be faulty, even if he had placed indium correctly. The insertion of indium between phosphorus and arsenic caused the latter elements to fall into octaves; it should be obvious that insertion of another element in a similar way would disrupt whatever octaves already existed. The point here is not a simple misclassification, a problem which beset even Mendeleev; it is the logical necessity of misclassification when new elements or new atomic weights are discovered. In a system with no empty spaces, the only ways an octave relationship can be preserved upon the discovery of an intervening element is for that element to share a position already occupied (a possibility in Newlands’ classification, albeit one he did not emphasize) or to displace an already existing element from its position in the table. In the latter case, there must be some error in classification, either before or after the new element takes its position.

An attempt of systematization can be seen in Newlands’ 1878 article in the *Chemical News* (18) and the introduction to his 1884 monograph (7). In addition to asserting his priority in formulating the periodic law, he provided a checklist of specific instances in which he applied that law. This striving for system came late, and, in my judgment, actually accentuates the lack of organization among his many and substantial contributions. The items on the list are drawn from several papers, including items, such as the prediction of germanium, which predate the law of octaves or whose connection to it is tenuous at best. One item on the list, his prediction of the atomic weight of the newly discovered element indium, was hardly unequivocal (30):

The equivalent of indium, then, may prove identical, or nearly so, with those of zinc or cadmium. ... It is also just possible that indium may occupy a position in the zinc group similar to that of thallium among the alkali metals, in which case the equivalent of indium would be 182, or thereabouts.

In fact, he ended up incorporating indium into his table just before arsenic. Several of the items on the list of applications were not original, such as recognizing the superiority of Cannizzaro’s atomic weights, attempting to explain numerical relations between atomic weights,
and (as already noted) ordering the elements by atomic weight. Newlands’ collection of applications culled from various papers is clearly deficient by comparison with Mendeleev’s extensive list of deductions which accompanied his periodic system from the outset (17, 21).

The close juxtaposition of articles in Newlands’ monograph (7) also accentuates their lack of continuity. For example, in the second of two articles (15) on relations among atomic weights, he referred to the relationships he established in the earlier article—even though the two articles involve different sets of atomic weights (14)! That is, in the second paper he specifically cited the first paper’s atomic weight relationships among related elements (e.g., lithium, sodium, and potassium; or chlorine, bromine, and iodine) without noting that in the second paper he employed a different system of atomic weights. The two articles originally appeared a year and a half apart, but their proximity in the monograph underlines the discontinuity of atomic weight systems despite the constancy of conclusions.

**Assessment with Lachman’s Criteria**

Because Newlands’ contributions lack systematic organization, his work does not fare highly with respect to Lachman’s criteria of clarity or coherence. Newlands was undoubtedly misunderstood in his day and continues to be today. At least part of this persistent misunderstanding can be attributed to incomplete or unsympathetic reading. The notion that the fanciful name “law of octaves” prevented Newlands’ contemporaries from taking his work seriously has become commonplace (31). As noted above, the idea that the rows in his tables are co-extensive with chemical families is a misreading, and the criticism by one of his contemporaries that consecutive elements such as iron, nickel, and cobalt are assigned to different groups was likewise a misreading. Even Mendeleev confused Newlands’ octaves with groups of related elements (32); but Newlands’ poor exposition of his ideas must surely bear part of the blame for some misunderstandings.

Newlands’ work does not measure up well against Lachman’s criterion of precision of prediction. Although Newlands’ clarifications of the misreadings just mentioned prevent some incorrect deductions from being made from his law of octaves, they greatly reduce the possibility of making any deductions from the law. For example, stating that “elements belonging to the same group usually appear on the same horizontal line” does not allow the reader to deduce which, if any, of the elements in the same horizontal row as nitrogen belong to its chemical family. Newlands also noted “that elements having consecutive numbers frequently … belong to the same group (16).” Thus the classification leaves open the possibility that nitrogen is related to carbon or oxygen. Newlands knew precisely which elements were related to nitrogen; however, his classification does not specify that knowledge. For this reason, the classification does not earn a high rating for completeness either. (In another sense the classification was complete, however, for it included every element known at the time.)

Simplicity is another criterion in which Newlands’ work earns a mixed rating. On the one hand, the law of octaves and the tables which embody it are simplicity itself: order the elements by atomic weight, filling a table which contains seven rows. Even the instruction to put two elements in the same space if their atomic weights were close enough is simple. The few inversions in atomic weight order (Table II contains fewer than Table I) are not simple, however, even where they are correct (such as placing iodine with the halogens and tellurium with the chalcogens). As just noted, knowing which elements are a part of groups, among the candidates simply identified by the table, is not simple at all.

Finally, Newlands’ work must be ranked low in fruitfulness. This criterion is unlike Lachman’s others in looking beyond the theory itself to its reception by other scientists. By all accounts, Newlands’ work was not influential in the development of the periodic system used today. Neither Mendeleev nor Meyer, the two scientists honored in 1882 with the Davy medal for their work on the subject, was influenced by Newlands.

Close examination of Newlands’ work is worthwhile not only as an interesting episode in the history of chemistry but also as a case study in the development of an area in science. Normal progress in science is rarely systematic. Observations from a variety of sources, often seemingly unrelated, are accumulated in a somewhat random manner. The scientific community does not require that each new piece of information be explained before it is published. Indeed, such a requirement would be counterproductive, effectively stifling the cross fertilization of ideas in which one investigator follows up on an anomaly first reported by another. Seen in this context, Newlands’ work is solid, original, and important.

The great discoveries in science, however, often involve syntheses, explanations of a body of informa-
REFERENCES AND NOTES

2. In 1998, the centenary of his death, Newlands was the subject of a symposium of the Royal Society of Chemistry; and his home was designated a historic place.
7. J. A. R. Newlands, On the Discovery of the Periodic Law and on Relations Among the Atomic Weights, E. & F.N. Spon, London, 1884. This brief monograph also includes reprints of Newlands’ communications on the subject previously published in the Chemical News.
chemistry: an Experimental Science, Wiley, New York, 2nd ed., 1995 (a popular work on chemical periodicity and an introductory chemistry textbook, respectively).


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FUTURE ACS MEETINGS

Spring 2000 — San Francisco, CA
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CHRISTLIEB EHREGOTT GELLERT AND HIS METALLURGIC CHYMISTRY

Fathi Habashi, Laval University

Introduction

Christlieb Ehregott Gellert (1713-1795) (Fig. 1) was the first professor of metallurgical chemistry at the Mining Academy in Freiberg on its foundation in 1765. His book Metallurgic Chymistry was first published in German in 1751 as Anfangsgründe der metallurgischen Chemie (Fig. 2). The book is a little known work although it is of special importance because it was written towards the end of the Age of Alchemy. It was also the first and last book combining chemistry and metallurgy, a course Gellert was giving at the Academy. His successor Wilhelm Lampadius (1772-1842) separated this course into two sections: one for chemistry and one for metallurgy (1). The book, therefore, provides a glimpse at a critical period in the history of chemistry and metallurgy, with use of the alchemist symbols and adherence to the phlogiston theory.

Gellert was born on August 11, 1713 in Hainichen, a suburb of Freiberg, as the son of the town pastor, and he died May 18, 1795 in Freiberg; he never married (2-5). He studied at Meissen and Leipzig. From 1735 to 1747 he was professor in a secondary school in St. Petersburg (6) and at the same time became associated with the Russian Academy of Sciences. On his return to Freiberg he worked in private metallurgical practice as a consultant to the local smelters. A few years later he started private teaching of metallurgical chemistry at his home to fill the gap created by the death of Johann Friedrich Henckel (1679-1744), who was the first to found in 1735 in Freiberg a private School of Mines (7). Gellert restored to Freiberg its precious fame as a center for teaching metallurgical chemistry, and it became the goal of the local and foreign students. For example, because of his fame as the best metallurgical chemist of his time, the King of Sardinia sent him five students. In 1753 he was appointed Inspector of Mines and Smelters in Saxony, and in 1762 he became Chief Administrator of Foundries and Forges of Freiberg before accepting the teaching position at the newly founded Mining Academy.

In 1746 while in St. Petersburg he translated Cramer’s book (8) Elementa Artis Docimastica into German as Anfangsgründe der Probierkunst (682 pages) and in 1750 wrote his own work Anfangsgründe der metallurgischen Chemie and
in 1755 another work Anfangsgründe zur Probierkunst, both published in Leipzig. Both were translated in 1758 into French by the philosopher Baron Paul-Henri Dietrich d’Holbach (1723-1789) and published in Paris under the title Chimie métallurgique in two volumes. Italian translations appeared in 1758 and 1790. Gellert is credited with being the first to realize that the melting point of a mixture of two oxides is lower than that of either oxide taken separately. This is, of course, important in the formation of slags during a smelting process. He also measured the density of alloys and concluded that this was mostly greater than that calculated by the mixture rule.

The metallurgy of gold and silver played an important role in the development of chemistry before the Industrial Revolution. While the action of mercury on gold and the formation of amalgams were known to the Romans, this knowledge was applied for the first time on an industrial scale to recover silver from its ores in Mexico and the Spanish South American colonies in the middle of the sixteenth century. In Europe silver was mainly recovered from sulfide ores by smelting. Interest in the Spanish practice was aroused in Europe as a possibly cheaper technology. The Austrian mineralogist Ignaz von Born (1742-1791) tested this possibility by what became known later as the “chloridizing roasting process.” The silver sulfide ore, which is not amenable to direct amalgamation, was first roasted with salt and then slurried with water and mercury to make silver amalgam from which silver could be recovered. The process was improved by Gellert and applied on an industrial scale in a plant near Freiberg, which operated from 1790 to 1857 and produced more than 300 tons of silver.

Gellert’s Main Work

Gellert broke the tradition of his time by writing in German instead of Latin. His first book was translated into English in 1766 as Metallurgic Chymistry by John Seiferth, apparently at the request of the Royal Society in London (10). The English translation, however, was not printed until ten years later. This is deduced from the first few pages of the book which carry a message “To the President and Members of the Royal Society,” dated August 20, 1766, followed by another message “To the Reader,” dated June 4, 1776; both messages were signed by the translator. In the introduction, Gellert refers to the sources he used. Although he quotes the names of Becher, Stahl, Henckel, Pott, Marggraf, and Cramer, he does not cite the titles of their works nor any other details. Also in the text (p 375) he refers to Agricola and Schlüter without citing their works (11).


The first division of the Theoretical Part can be compared to modern mineralogy, ore deposits, and properties of metals (very briefly). The second division is a discussion of the four chemical agents: fire, air, water, and earth which are usually and erroneously described in history of chemistry books as the “Four Elements.” Gellert clearly states that “fire is the principal agent in the art of chemistry; without its assistance no chemical operation can be performed.” Concerning air, he argues that, “Since no chemical operation may be done without fire, it follows that they can neither be performed without air.” He emphasises further that no fire can exist without air, and nobody known could live and grow without air. Gellert states that “Water has that peculiar property of uniting with other bodies and to constitute

Figure 2. Gellert’s Anfangsgründe der metallurgischen Chemie (1751)
therefore so perfect a mixture....” Further, he defines earth as “a simple, hard, fixed, friable body, not fluxing in the fire, and neither soluble in air nor water, nor spirits of wine, nor in any oil.” With these statements Gellert makes sense of the so-called four elements which are usually ascribed to Aristotle but in reality were known earlier to the Persian prophet Zoroaster (660-583 B.C.? ) as the four sacred elements (12).

In addition to the four agents, Gellert devotes an appreciable space to “Dissolvent Menstrua.” This is a general term which in modern terminology could be equivalent to fluxes, to acids forming aqueous solutions, and to metals forming alloys. Gellert then devotes a chapter to chemical apparatus, mainly furnaces. Here he refers to books by Boerhaave, Cramer, and Ludolph, but without citing the exact works (13). The chapter contains numerous illustrations combined in four charts, one being devoted to laboratory utensils such as the alembic (a distillation flask), and tongs, the other three to furnaces.

Chemical operations discussed in the third division are classified according to the four agents. Thus, operations performed by fire include fusion, roasting, calcination, sublimation, distillation, and evaporation. Those performed by air, are described, such as “solution of metals by the air” (oxidation ?), fermentation, putrefaction, and others. Those performed by water, are washing, elixiviation (leaching), and edulcoration (purification by washing). An operation performed by earth is fixation. In addition, Gellert cites chemical operations performed by means of “Dissolvent Menstrua,” which include amalgamation, solution in the dry way like glass making, making of brass, soldering, scorification (formation of slag), reduction of “metalline calces into metal,” and “solution in the liquid way.” For these operations, Gellert modifies Geoffroy’s Affinity Table constructed in 1718.
without any reference to his predecessor. Both Tables are shown in Fig. 3 and 4 for comparison. Gellert’s Table, with 28 columns and 18 rows, was more elaborate than that of Geoffroy, which was constructed of 16 columns and 9 rows. Gellert placed substances having the least affinity with the substance at the head of a column at the top, the reverse of Geoffroy’s order. He included a list of “Chemical Figures”, i.e., symbols for fire, air, water, earth, acid, alum, metals, etc. He used few letter symbols in the table: cobalt = K, bismuth = W (for Wismut in German), zinc = X. A calx (oxide) is shown by prefixing C, e.g. CX (calx of zinc), CW (calx of bismuth).

The experiments mentioned in the second part of the book were apparently supposed to be conducted by students. Each experiment has a number, a title, and is divided into two parts: Method and Observation. Sometimes more than one method is described for the same experiment. Although they are written in a systematic way, there was no attempt to group related experiments together. Most of the experiments are inorganic in nature; that is, related to metals, salts, and stones. Among the very few are organic experiments is the preparation of soaps from an oil. The modern reader would classify these experiments approximately as follows: preparation of salts, e.g., ferrous sulfate from pyrite, alum from alum ore, saltpeter from a nitrous earth, etc.; preparation of acids, e.g., sulfuric acid by distillation of ferrous sulfate, nitric acid from saltpeter, hydrochloric acid from common salt, aqua regia, etc.; preparation of alloys; melting of two oxides; dissolving metals in a variety of solutions; dissolving minerals in a variety of solutions; and precipitation of a variety of compounds from aqueous solution.

**Chemistry, Metallurgy, and Metallurgical Chemistry**

Freiberg, an important mining town, is located 40 km southwest of Dresden. It was the capital of the mining
district of Saxony and the seat of the Mining Academy, which is the oldest school of mines that is still functioning in its original location. It is an ancient imperial city that owes its origin to the discovery of silver mines in its vicinity in the twelfth century. The mining district is known as Erzgebirge or Ore Mountains, the mountain chain that separates the present Czech Republic from Germany. These mining schools played an important role in the advancement of chemistry and metallurgy. Chemistry was taught in mining schools much earlier than in Philosophical Faculties. The Mining School of Potosi in the Spanish colony of Peru already had a chair in chemistry in 1757 (14). Customarily in Europe, chemistry was taught in medical schools, and it was Wolfgang von Goethe, while education adviser to the Grand Duke Carl August the Elector of Jena, who created the first chair of chemistry in the Philosophical Faculty of the University of Jena in 1810. Goethe supplied Johann Friedrich Gottling (1755-1809) with a professorship in chemistry and pharmacy at the University of Jena in 1789 with salary, i.e., before the full chair was founded (15). As early as 1764, pyrometallurgy and fire assaying were taught systematically at the Mining Academy in Schemnitz (16). Pyrometallurgy was known in German as Metallhüttenkunde while fire assaying as Probierkunde, and both were known collectively as Metallurgical Chemistry.

<table>
<thead>
<tr>
<th>Year published</th>
<th>Author</th>
<th>Title</th>
<th>Contents</th>
</tr>
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<tbody>
<tr>
<td>1530</td>
<td>Agricola</td>
<td>Bermannus</td>
<td>Conversation with a miner and mineralogist</td>
</tr>
<tr>
<td>1533</td>
<td>Agricola</td>
<td>De Mensuris et Ponderibus</td>
<td>Greek and Roman weights and measures with some correlation to those used in Saxony</td>
</tr>
<tr>
<td>1546</td>
<td>Agricola</td>
<td>De Natura Fossilium</td>
<td>A treatise on minerals</td>
</tr>
<tr>
<td>1546</td>
<td>Agricola</td>
<td>De Veteribus et Novis Metallis</td>
<td>Historical and geographical references to the occurrence of metals and mines, and history of mines in Central Europe</td>
</tr>
<tr>
<td>1546</td>
<td>Agricola</td>
<td>Retum Metallicarum interpretation</td>
<td>A collection of about 500 Latin terms in mineralogy and metallurgy with their German equivalent</td>
</tr>
<tr>
<td>1546</td>
<td>Agricola</td>
<td>De Orlu et Causis Subterraneorum</td>
<td>Views on geological phenomena</td>
</tr>
<tr>
<td>1546</td>
<td>Agricola</td>
<td>De Natura eorum quae Effluunt ex Terra</td>
<td>A short account on substances which flow from the earth, e.g., water, gases, and bitumen</td>
</tr>
<tr>
<td>1549</td>
<td>Agricola</td>
<td>De Animantibus Subterraneis</td>
<td>A short work on animals that spent a portion of their life underground (serpents, lizards, etc.)</td>
</tr>
<tr>
<td>1550</td>
<td>Agricola</td>
<td>De Precio Metallorum et Monetis</td>
<td>Description of mining, comparison of different coins and their value</td>
</tr>
<tr>
<td>1556</td>
<td>Agricola</td>
<td>De Re Metallica</td>
<td>A treatise on prospecting, mining, assaying, beneficiation, smelting, and other topics</td>
</tr>
<tr>
<td>1556</td>
<td>Ercker</td>
<td>Probierbüchlein</td>
<td>Assaying</td>
</tr>
<tr>
<td>1574</td>
<td>Ercker</td>
<td>Beschreiburg aller-fürnemisten mineralischen Ertz und Berckwercks - arten</td>
<td>Treatise on mining, ores, and assaying</td>
</tr>
</tbody>
</table>

*Table 1.* First major books published in Central Europe related to geology, mining, and metallurgy.

Mining and metallurgy were among the most profitable undertakings of the period. This was true especially at Freiberg in Saxony. The silver-bearing lead deposits in the Erzgebirge, discovered about the end of the twelfth century, proved so much richer in silver than the similar ores of the Harz Mountain district, that a mining rush to the Erzgebirge took place. The outcome
of this was that by the end of the sixteenth century it was the most highly developed mining district of Europe. The production of metals, especially of gold and silver, was usually a source of important income to the ruling sovereign, no matter upon whose land they were discovered. The practical procedure under this system was to grant to a discoverer the right to work the deposit on payment of a "royalty" to the legal owner of the land. This, in turn, made it necessary for the owner to exercise some supervision over the producer, to ensure he was not being cheated of his rightful dues, either through dishonesty or inefficiency, in the actual operation of the enterprise. Such supervision required a thorough knowledge of mineral technology.

The basic writings or mining, metallurgy, and geology, appearing in Central Europe in the beginning of the sixteenth century, were responsible for transmitting this knowledge for future generations. Among the most important of these books are those by Georgius Agricola (1440-1555) and Lazarus Ercker (1530-1593) (Table 1). Agricola, a medical doctor in Saxony who practiced medicine in the mining district of Joachimsthal, became interested in ores and smelting operations. Ercker, also from Saxony, was the assay master at Dresden and later director of the mint in Kutna Hora in Bohemia. It is no wonder then that many small vocational mining schools were created in Central Europe to teach this art.

There was scarcely any systematic education in other branches of chemistry before 1800. They were generally an adjunct to medicine if they were taught at all at a university. Chemistry was best learned, not in a university but in a pharmacist's shop. Fire assaying, the predecessor of analytical chemistry of today, was taught at the Mining Academy from both a theoretical and experimental standpoint. This method of teaching in Schemnitz was adopted in 1794 in the École des Travaux Publics, later the École Polytechnique in Paris by Antoine François de Fourcroy (1755-1809), who wrote (17):

La physique et la chimie n'ont été montrées qu'en théorie en France. L'École des mines de Schemnitz en Hongrie nous fournit un exemple frappant de l'utilité de faire exercer ou pratiquer par les élèves les opérations qui font la base de ces sciences utiles. Des laboratoires y sont ouverts et munis des ustensiles et des matériaux nécessaires pour que tous les élèves y répètent dans leurs unions. Le Comité du salut public a pensé qu'il fallait introduire dans l'École des travaux publics cette méthode.

When Justus von Liebig (1803-1873) became Professor of Chemistry at Giessen in 1824, he immediately took steps to offer laboratory instruction in the science in the same way as he himself had received instruction in Paris. Students were first trained in qualitative and quantitative analysis; then prepared organic compounds, and finally carried out a special investigation on a problem suggested by Liebig. The laboratory at Giessen received a great deal of attention and attracted students from many parts of the world.

The teaching staff at the first school of mines contributed greatly to the advancement of mining and geology as well as chemistry and metallurgy. They analyzed and discovered many new minerals, discovered eight metals (Table 2), and created the basic literature in chemistry, metallurgy, mining, and geology. The German and

<table>
<thead>
<tr>
<th>Year</th>
<th>Metal</th>
<th>Discoverer</th>
<th>School</th>
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<tbody>
<tr>
<td>1783</td>
<td>Tungsten</td>
<td>D' Elhuyar</td>
<td>Vergara, Spain</td>
</tr>
<tr>
<td>1797</td>
<td>Beryllium</td>
<td>Vauquelin</td>
<td>Paris</td>
</tr>
<tr>
<td>1797</td>
<td>Chromium</td>
<td>Vauquelin</td>
<td>Paris</td>
</tr>
<tr>
<td>1789</td>
<td>Uranium</td>
<td>Klaproth</td>
<td>Berlin</td>
</tr>
<tr>
<td>1789</td>
<td>Zirconium</td>
<td>Klaproth</td>
<td>Berlin</td>
</tr>
<tr>
<td>1801</td>
<td>Vanadium*</td>
<td>del Rio</td>
<td>Mexico City</td>
</tr>
<tr>
<td>1863</td>
<td>Indium</td>
<td>Reich and Richter</td>
<td>Freiberg, Saxony</td>
</tr>
<tr>
<td>1886</td>
<td>Germanium</td>
<td>Winkler</td>
<td>Freiberg, Saxony</td>
</tr>
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* Independently discovered by Sofström at Falun, Sweden in 1830.

Table 2. Metals discovered by teaching staff at the first schools of mines.
Austrian professors were particularly prolific. Their writings were influential up to World War I; a serious student must learn German to be able to make use of this vast heritage.

Epilogue

Metallurgical chemistry is the oldest branch of chemistry. Gellert mentioned the seven ancient metals: gold, silver, copper, iron, tin, lead, and mercury, the two new metals, zinc and cobalt, as well as the three metalloids: arsenic, antimony, and bismuth. But, he did not mention platinum although this metal should have already become known in Europe. Metallurgical chemistry became the basis of the emerging branch of metallurgy known today as extractive metallurgy, i.e. the extraction of metals from their ores which can be conveniently divided into three sectors:

Thermal methods: pyrometallurgy, e.g., oxidation, reduction, melting, chlorination, fluorination, etc.

Wet methods: hydrometallurgy, e.g., leaching, filtration, solution purification, ion exchange, solvent extraction, precipitation, etc.

Electrolytic methods: electrometallurgy, e.g., electrowinning and electrefining, from aqueous solutions and fused salts.

Metallurgical chemistry requires a thorough knowledge of inorganic chemistry, mineralogy, and chemical engineering. The challenge facing extractive metallurgists today is the fact that ores are becoming poorer and poorer while the need is increasing to prepare purer and purer metals. Furthermore, the necessity of avoiding pollution of the environment and of incurring the minimum expenditure of energy during these operations is essential. Hence new chemical reactions are continuously being examined to uncover the most efficient process. Metallurgical Chymistry was the starting point in this direction.

REFERENCES AND NOTES

6. Saint Petersburg was founded in 1703 by Peter the Great as the capital of Russia. Moscow replaced it as the capital in 1918. Its original name was restored after the fall of the Communist Party in 1991. The Academy of Sciences was founded in 1724 and attracted many foreign scientists, for example the Swiss mathematician Leonhard Euler (1707-1783) with whom Gellert became associated.
7. Henckel was born on August 11, 1679 in Merseburg in Saxony, studied medicine in Leipzig, and practiced his profession in Freiberg for a short time when he became interested in mineralogy, chemistry, and metallurgy. He gave up medical practice in 1732 when he received a contract from the state to look for and evaluate the mineral deposits of Saxony. He published Pyritologia in 1735 in which he discussed smelting processes. In the same year he was given another contract to found a chemical laboratory to teach mineralogy and metallurgy. The laboratory became famous and well attended by many students who came from Sweden, Norway, and Switzerland, as well as from other parts of Germany. He wrote a textbook for his students which was published after his death. It was translated into French in 1756 under the title Introduction à la Minéralogie. It was composed of two parts: the first dealing with minerals and the second with metallurgical chemistry. He died in Freiberg on January 26, 1744.
8. Johann Andreas Cramer (1710-1777) was born in Quedlinburg, studied medicine and chemistry, then turned his attention to assaying. He gave lectures in London and Leyden. In 1739 he published his book Elementa artis docimasticae (second edition, 1744) which was translated into several languages. From 1743-1773 he served as Mining and Smelting Adviser in Braunschweig. During this period he published his three-volume work Anfangsgründe der Metallurgie (1744-1747). He was considered the best assayer of his time and his books were widely used.
10. Full title: Metallurgic Chymistry. Being a System of Mineralogy In General, and of all the Arts arising from this Science. To the great Improvement of Manufactures, and the most capital Branches of Trade and Commerce. Theoretical and Practical Translated from the original
German by John S[eiferth]. A facsimile edition was published in 1998 by Métallurgie Extractive Québec, 800 rue Alain #504, Sainte-Foy, Québec, Canada, G1X 4E7 (ISBN 2-9803247-3-6), with an introduction by Fathi Habashi, available from Laval University Bookstore. Fax (418) 656-2665.

11. The names cited by Gellert are famous chemists who published numerous books on chemistry. Their full names, years of birth and death are only given here: Johann Joachim Becher (1635-1682), Georg Ernst Stahl (1660-1734), Johann Friedrich Henckel (1679-1744), Johann Heinrich Pott (1692-1777), Andreas Sigismund Marggraf (1709-1782), Georgius Agricola (1494-1555), Christopher Andreas Schlüter (?).


13. Other famous chemists and their books cited by Gellert: Hermann Boerhaave (1668-1738) professor in Leyden, who wrote Elementa Chemiae in 1732. His equipment and works are preserved at a museum bearing his name in his home town. Nothing could be found about a chemist named Ludolph. However, Ludolph Ceulen (1539-1610) is cited in Poggendorff as professor of mathematics in Amsterdam and Leyden. For Cramer, see Ref. 8.


16. The Mining Academy in Schémnitz was founded by Maria Theresa in 1762, at that time a part of the Austrian Empire. The school was closed after the dismantlement of the Empire following the end of World War I. Schémnitz is now known by its Slovak name Banska Stiavnica.

17. “Physics and chemistry have formerly only been taught from a theoretical basis. The Schémnitz Mining School has illustrated the usefulness of teaching the practical operations which are, after all, the basis of our science. By providing the students with apparatus and chemicals, they are able to reproduce for themselves the phenomena of chemical combination. The Committee for Public Welfare is of the opinion that these methods should be introduced at the École polytechnique.” Journal de l’École Polytechnique (1795); Gazette nationale ou Moniteur universel No. 8 Oktidi 8, Vendémiaire; quoted by F. Szabadvary, History of Analytical Chemistry, Pergamon Press, Oxford, 1966, 45.

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With the start of the 20th century, clinical chemistry emerged into its own space on the mosaic of medical practice. The pattern of its future growth and development took shape during the first two decades of the new century, the United States leading the way with the decisive breakthrough. Until then the United States had played no role in the growth or development of clinical chemistry. Afterward, the nation quickly achieved leadership which it never relinquished.

Two names dominated this period, as their papers filled the pages of the Journal of Biological Chemistry and other publications: Otto Knut Folin (1867-1934) and Donald Dexter Van Slyke (1883-1971). Their systematic explorations on blood and urine set the style and shaped the parameters for clinical chemistry for the remainder of the century as they developed practical and clinically applicable methods of analysis. On the basis of a new approach to methodology—analysis of small volumes of biological fluids—they determined normal ranges, correlated variations with pathological conditions, and elucidated metabolic pathways in health and disease. Neither Folin nor Van Slyke held medical degrees; yet their research and teaching of biochemistry and clinical chemistry demonstrated that chemists could make great contributions to advances in medical diagnosis and the treatment of disease.

The Flexner Report and Medical School Reform

Folin and Van Slyke received a valuable assist in the development of clinical chemistry from an unlikely and unexpected source, the “Flexner Report.” Abraham Flexner (1866-1959), a former Louisville, Kentucky high school teacher and educator, had published his first book, The American College (1908), in which he severely criticized some of the current educational practices. The book drew the attention of Dr. Henry S. Pritchett, president of the recently established Carnegie Foundation for the Advancement of Teaching, and he asked Flexner to make a study of American medical schools. Flexner asked whether he was being mistaken for his brother Simon, director of the recently formed Rockefeller Institute for Medical Research in New York. Pritchett replied that he wanted an educator’s evaluation, not that of a medical practitioner. Published in 1910, the report exposed the disgraceful practices of the American (and Canadian) medical school systems and made specific recommendations for correcting the deficiencies. The report had a far-reaching effect on the practice of science in the laboratories of medical schools and hospitals and on the research and teaching of biochemistry.

Flexner specifically referred to “clinical chemists” and “clinical chemistry.” Concerning the laboratories connected with the university hospital, he wrote (2):

To suffice for clinical investigation the laboratory staff must be so extended as to place, at the immediate service of the clinician, the experimental pathologist, experimental physiologist, and clinical chemist in position to bring all the resources of their several departments to bear on the solution of concrete clinical problems. Of these branches, experimental pathology and physiology have already won recognition; the next step in progress seems to lie in the field...
of clinical chemistry, thus far quite undeveloped in America.

His emphasis on the use of laboratory sciences in the training of medical students and in the teaching of specialties contributed to the favorable environment for the rapid growth of clinical chemistry. Flexner’s views complemented and reinforced what Folin had said two years earlier to the Harvey Society. Folin reminded the medical profession of the large variety of clinical material available for biochemical investigations in the large city hospitals. If these hospitals are to become centers for biochemical research, as they should, according to Folin, they must provide laboratory facilities, personnel, and independence to the trained chemist to work on the many biochemical problems seeking answers (3).

**Otto Folin**

Otto Folin was 15 years old when, at his mother’s urging, he left home in Sweden in 1882 to join his older brother in Minnesota. What followed is the familiar American success story. Immigrant boy arrives penniless and in debt, works as unskilled laborer, learns English and the new customs, acquires an education, and becomes a professor at Harvard (4). Folin graduated from the University of Minnesota and entered the University of Chicago for graduate study in 1892, the year it opened. At Chicago, he completed his doctoral work on urethanes under Julius Stieglitz (1867-1937) in 1896. Then, acting on the advice of the eminent physiologist, Jacques Loeb (1859-1924), Folin decided to take additional training in Europe in the newly emerging field of physiological chemistry, which barely existed in the United States. Six months of the first year, 1896-97, was spent in the laboratory of Olof Hammarsten (1841-1932) at the University of Uppsala, not far from Folin’s childhood home. Here he examined the properties and composition of a hydrolysis product of a glycoprotein, mucin, from submaxillary glands. A short paper on this subject was published in Hoppe-Seyler’s Zeitschrift für Physiologische Chemie in 1897 (5). It was Folin’s first contribution to biochemistry.

During the summer of 1897 he worked in the Berlin laboratory of Ernst Leopold Salkowski (1844-1923). There, his first contact with hospital patients led to an interest in the urinary end products of nitrogen metabolism. He improved a quantitative method for urinary uric acid and published it in 1897 as sole author (6). The analysis of uric acid remained a lifelong interest. Six months of the next year, 1897-98, was spent with Albrecht Kossel (1853-1927) in Marburg, where he applied his knowledge of organic chemistry to biological problems and where his interests in the intermediary stages of protein metabolism had their beginning. Two more papers appeared in Hoppe-Seyler’s Zeitschrift (7, 8). It was at Marburg that he discovered the new technique of colorimetry used in the brewing industry and the color comparator invented by Jules Duboscq (1817-1886). This instrument was to become the basis of his major contributions to developing simple, reliable, and convenient colorimetric methods for clinical chemistry. On his return to Chicago in 1898 he was awarded the Ph.D.

There were no academic positions available in physiological chemistry in the US. In the few universities and medical schools where this subject was being taught, it was assigned to instructors in physiology, pharmacology, or medical chemistry. Only Yale had a department of physiological chemistry, established in 1882 by Russell Chittenden (1856-1943) (9). Consequently, Folin accepted a position as chemist in a private, commercial laboratory in Chicago, specializing in analysis of water, food, and medical products and in toxicology. A teaching opportunity came in the summer of 1899. He accepted an assistant professorship of chemistry at
West Virginia University, where he offered courses in quantitative analysis and elementary physiological chemistry.

Metabolic Studies at McLean Hospital

In 1900 Folin received an offer from the McLean Hospital in Waverley, Massachusetts, a suburb of Boston. Edward Cowles (1837-1919), the medical superintendent of this private psychiatric hospital, had established a laboratory for physiological chemistry in 1889, one of the first of its kind in the US to support research. His objective was to advance the understanding of mental diseases by searching for a connection between abnormal mental states and urinary excretion, especially of urea and uric acid. Cowles believed, as did others, in a correlation between insanity and chemical toxins produced by faulty metabolism and poor nutrition. He expected to find evidence of this in the patient's urine. Research conducted by resident physicians was begun in 1891-92. Blood changes in hemoglobin, red and white blood cell counts, differential count of white cells, and specific gravity were also studied. When larger laboratory facilities were built in 1895, Cowles planned a special research department to be run by a professional biochemist. Folin was asked to plan, equip, and develop his own program of research toward achieving Cowles' objective: uncovering an association between mental status and urinary excretion (10).

Nineteenth-century clinical chemistry involved chiefly the examination of the urine. This was understandable; its collection offered no technical difficulties or risks, and the quantities of fluid available allowed utilization of the gross methods of gravimetric and volumetric analysis already in use and requiring large volumes of specimen. The objective at that time was to isolate the particular substance in pure form, then weigh it or titrate it.

Finding no evidence of toxicity in urine of insane patients, as was claimed by some French writers, nor of qualitative differences, Folin turned to the study of protein metabolism of normal versus mentally disturbed individuals by measuring as accurately and completely as possible all of the known nitrogenous and other products excreted in the urine of patients fed a standard diet. He would thereby establish the normal range of the nitrogenous fractions and then consider whether differences were due to an abnormal metabolism in mental disease. Normal patterns were then unknown. To establish norms would by itself be an important undertaking; but first, he had to devise additional and improved quantitative methods before any survey could be initiated. This was to lead to his lifelong interest in quantitative methods for nitrogenous end products in urine.

When Folin began his detailed studies of nitrogen metabolites in urine, there was no commercial source of purified chemicals, water, standards, calibrated glassware, or instruments designed for use in the clinical chemistry laboratory. Procedures for testing of urine—mostly qualitative, some quantitative—filled major portions of books on clinical diagnosis by laboratory methods. Practical quantitative chemical analysis of blood was virtually nonexistent or was described only briefly. The development of blood chemistry was hampered by a shortage of blood for experimental and diagnostic purposes, as a result of the gradual abandonment of bloodletting as a therapy late in the 19th century. Large volumes of blood were required for chemical analysis and there was no well developed or convenient technique for drawing the large amounts needed. Furthermore, the plasma proteins (and red cells) interfered markedly with the methods; consequently, blood was rarely tested. Hematological procedures, on the other hand, namely, blood counts, hemoglobin, and white cell differential, were readily supplied by finger stick.

The first years at McLean were spent mainly in devising and testing methods for the determination of nitrogenous constituents in urine, most of which were known qualitatively, e.g., urea, ammonia, uric acid, creatinine, and creatine. Previously, quantitative methods for these constituents were frequently laborious or complicated and, as in the case of urea, were nonspecific; or in the case of uric acid, they required relatively large amounts of specimen. Folin's first colorimetric method was developed for urinary creatinine in a reaction with picrate ion in alkaline medium at room temperature to form a red color. Color comparison was made with an artificial standard—N/2 potassium bichromate—after correlation with pure creatinine had been established. Although other color reactions had been used long before this to estimate biological products, e.g., Nessler's reagent for ammonia in water analysis, Folin's use of the Duboscq colorimeter for color comparison in the quantitative analysis of creatinine in urine in 1904 ushered in the modern era of clinical chemistry (11). The color reaction, discovered by Max Jaffe (1841-1911) in 1886 (12), is the longest continuously used colorimetric procedure for blood or urine analysis; and until 1936, when the reaction with 3,5-dinitrobenzoic acid was described (13), it was the only method for creatinine.
Folin's studies at the McLean Hospital revealed no metabolic evidence related to mental disease, but in the course of his work he had developed methods for biochemical research that promised to deliver significant results of a more general physiological interest and importance. While at McLean, a personal misfortune struck Folin. In the spring of 1903 a benign tumor was removed from his left parotid gland. During the surgery it was necessary to cut the facial nerve. This procedure permanently altered Folin's appearance.

**Colorimetric Methods for Blood Analysis**

Folin's simple colorimetric method for the quantitative estimation of urine creatinine in 1904 was the breakthrough that opened up the possibilities of this rapid, simple, and inexpensive technique for analysis. It gave great impetus to the development of additional methods for quantitative analysis of other nonprotein nitrogen products in urine. The increased sensitivity of colorimetric procedures allowed use of smaller samples and resulted in greater accuracy than was previously possible with the older gravimetric and volumetric (titrimetric) methods. What followed in laboratories in the US and abroad was the use of Folin's small-sample, reliable methods for the design of research protocols to study the composition of urine from normal individuals and patients with various disorders. However, the analysis of urine had limited clinical usefulness. It gave information primarily about the excretion of abnormal amounts of urine constituents.

Folin then turned to refining analytical methods to make them applicable to the same constituents in blood, but in much smaller samples than were required by other methods. He recognized that, since blood plasma reflected the condition of the extracellular fluids as a whole, blood analysis was a better guide to metabolic reactions and clinical evaluation of nephritis than was urinalysis. It was much more important to know what metabolic products the kidneys failed to excrete and accumulated at harmful levels in the blood, than it was to know what and how much was excreted in the urine (14). In 1914, ten years after introducing the alkaline picrate colorimetric reaction for creatinine in urine, Folin described the first satisfactory method for determining creatinine in blood. He published the first extensive data with this reaction for normal individuals and in various pathological states (15). Folin followed with colorimetric methods for urea, uric acid, creatine, ammonia, and nonprotein nitrogen in blood. These analyses served as a tool for quick and reliable assessment of the retention of the ordinary nitrogenous waste products caused by failing kidney function. Their practical value as an aid in diagnosis and determination of operative risk represented an important advance for medicine and surgery. Other investigators in America and Europe followed Folin's lead and modified his procedures or developed their own practical colorimetric methods.

**Folin Joins Harvard Medical School**

The publication of several papers on a new theory of intermediary metabolism of ingested protein, along with the growing popularity of his methods of chemical analysis, brought Folin to the attention of the biochemical profession. It led, no doubt, to his appointment in 1907 as associate professor of biological chemistry, and in 1909, as Hamilton Kuhn Professor of biological chemistry and head of the department at Harvard Medical School, the first nonphysician on the faculty. He remained at Harvard until his death in 1934, teaching biochemistry to first-year medical students and building his department into a center of graduate study and research with a strong emphasis on analytical methods and clinical applications. Two of his graduate students later won...
Nobel Prizes: James B. Sumner (1887-1955) in 1926 for the first crystallization of an enzyme, urease; and Edward A. Doisy (1893-1986), with Henrik Dam, in 1943 for the isolation and synthesis of Vitamin K. A third member of the department, George H. Hitchings, a teaching fellow for the 1929-30 academic year, would share a Nobel Prize in Medicine or Physiology in 1988 for his part in the discovery of important principles for creating a rational method of designing new compounds that selectively operate against various disease states. Other students were Walter Ray Bloor (1877-1966), who developed methods for the determination of cholesterol and other blood lipids; Philip A. Shaffer (1881-1960); and Cyrus H. Fiske (1890-1978), who, with Yellapragada SubbaRow (1895-1948), discovered phosphocreatine in 1927 and developed a popular method for serum phosphorus.

Folin's best known collaborator was Hsien Wu (1893-1959). In 1919 they published "A System of Blood Analysis (16)." Using tungstic acid as the protein precipitant, they combined a number of different analytical procedures into a widely used, simplified, and compact system of blood analysis on a protein-free filtrate. Prior removal of the blood proteins is necessary because they interfere with most added chemical reagents. This was a welcome response to the rapidly increasing number of chemical blood analyses being performed in hospitals and a landmark development in clinical chemistry. The tungstic acid protein-free filtrate was adopted worldwide and remained in use until the introduction of "automated" analysis in the late 1950s, when deproteinization was accomplished by dialysis and, in subsequent years, by other innovative technologies and methods that did not require prior removal of proteins.

Modern chemical analysis of small quantities of blood would have been impossible without the colorimetric methods developed by Folin and others. These procedures entailed some sacrifice of accuracy since the product to be analyzed was not isolated and the reaction occurred in a complex chemical milieu—even if the proteins were removed before the analysis. The methods were far from specific and the results obtained were often falsely high because of nonspecific substances which gave the same color reaction as the substance analyzed. In spite of the shortcomings of these early methods, however, the analyses were of distinct clinical use in the diagnosis of diabetes, uremia, gout, and other diseases.

Folin's new methods, based on visual colorimetry and small volumes of specimen, were a stimulus to the growth of clinical chemistry. This activity coincided with the beginning of the institutional reform of biochemistry during the first two decades of the 20th century. The professional prestige of biochemists was largely advanced by their success in developing diagnostic tests for the practicing physician.

Folin helped found the American Society of Biological Chemists in 1906 and served as its third president in 1909. After the establishment of the Journal of Biological Chemistry in 1905, he submitted most of his papers there. He joined the editorial committee in 1919, serving as chairman for many years.

In 1908 Folin proposed that American hospitals employ clinical chemists to advance "our ability to differentiate between the physiologic and the pathologic (17)." He cautioned that although hospitals should become involved in biochemical research, clinicians can neither do nor direct chemical work. Systematic biochemical research requires the "ingenuity, resourcefulness and critical judgment of the trained chemist (17)."

Much of the early work in methods and applications in clinical chemistry was published in the Journal of Biological Chemistry. To a large extent, during the first quarter of the century, biochemistry was clinical chemistry. The Journal of Laboratory and Clinical Medicine, founded in 1915, served as another major outlet. After the clinical chemists formed the American Association of Clinical Chemists in 1948, this organization began to publish Clinical Chemistry in 1955. It had been preceded in 1949 by Scandinavian Journal of Clinical & Laboratory Investigation and followed in 1956 by an international journal, Clinica Chimica Acta, based in the Netherlands.

Donald Dexter Van Slyke and the Rockefeller Hospital

Donald D. Van Slyke received his Ph.D. from the University of Michigan in 1907 in organic chemistry under Moses Gomberg (1866-1947), the discoverer of organic free radicals. Van Slyke, expecting to follow his father's career as an agricultural chemist, had actually been offered a job with the Bureau of Chemistry in Washington. The elder Van Slyke [Lucius Lincoln (1859-1931), Ph.D. University of Michigan, 1882 (Prescott)] was a chief chemist at the Geneva Agricultural Experiment Station in New York. A chance encounter between Lucius Van Slyke and Phoebus Aaron Theodor Levene (1869-1940) at an American Chemical Society meeting.
in 1907, however, led to a job offer from Levene at the newly formed Rockefeller Institute for Medical Research in New York (18). By 1913 the administrators of the Rockefeller Institute recognized that internal medicine was moving rapidly ahead along chemical lines. To guide this advance they believed that the hospital of the institute should now have an experienced chemist in a senior position to conduct his own research while serving as a general advisor to physicians on chemical problems. The chemist would have to develop an interest in medical problems and be temperamentally able to cooperate with physicians, for whom the patients came first. After studying the chemistry of proteins and amino acids and their analysis at the institute for seven years, Van Slyke was selected in 1914 to develop a department of chemistry in the hospital, related to clinical chemistry (19).

Although Van Slyke had no experience in clinical work, Simon Flexner (1863-1946), the director of the institute, was impressed by his training in organic chemistry and his publications in biochemistry. Through an arrangement by Levene, who had collaborated with Emil Fischer, Van Slyke spent a year in Berlin in 1911 working with Fischer (1852-1919) and Emil Abderhalden (1877-1950), publishing a paper with each (20, 21).

Biochemistry was in its infancy. Accurate methods for blood constituents in small specimens were just becoming available. The concentration and distribution of many of the inorganic constituents of the body were not known. Proteins were not yet regarded as chemical entities; enzymes had not yet been isolated and characterized; the existence of hormones and vitamins was suspected, but they had not yet been clearly identified. Although Van Slyke began his career as an organic chemist, his interest in physiological function in health and disease resulted in an acceleration of new knowledge and the development of quantitative clinical chemistry. Van Slyke's design of accurate analytical methods for measuring gas and electrolyte equilibria in blood and the transport of blood gases furthered the understanding of respiratory physiology in health and disease.

Institutional context was crucial to Van Slyke's success in integrating chemistry and clinical medicine, because the Rockefeller Hospital encouraged a cooperative attack on a problem from all sides—chemical, physiological, and clinical. Clinical problems provided opportunities to develop, extend, and improve analytical procedures; new techniques led to discoveries in the physiology of disease. Van Slyke's first clinical prob-
lem was one in diabetic acidosis. Severely ill diabetic patients, under the most efficient treatment (low-calorie diet) available in the pre-insulin days, sometimes developed acidosis which, by the time it had become clinically noticeable, progressed at a very rapid rate to a fatal coma. What was needed was a method for detecting earlier stages of the acidosis. Van Slyke began by defining acidosis in chemical terms, rather than in descriptive medical language. He devised an instrument and developed a simple, reliable gasometric method for measuring the carbon dioxide content of plasma or serum (25). This rapid and relatively simple test for quantifying blood acidity made it possible to anticipate and prevent the fatal acidosis. The instrumental method was soon adopted in most hospital laboratories in the US and Europe. It continued in general use well into the 1960s, when it was replaced by automated colorimetric methods for bicarbonate levels in plasma or serum. Van Slyke’s technique for studying acidosis by using quantitative biochemical analysis dramatically increased understanding of the disease processes and provided a basis for rational treatment before the discovery of insulin. Van Slyke made fundamental contributions to the understanding of buffer action, acid-base balance, fluid and electrolyte equilibrium, and carbon dioxide transport by hemoglobin and oxyhemoglobin. He developed a method for determining clearance of urea from the blood and a rapid procedure for the determination of red cell, hemoglobin, and plasma protein concentration—under battlefield conditions—by measurement of specific gravity. His elegant yet precise and accurate analytical methods produced quantitative data that clarified the physiological and pathological states of humans.

Van Slyke was as influential as a teacher in the hospital laboratory as Folin was in the medical school. Although Folin trained more professional biochemists, Van Slyke’s wide-ranging investigations of disease states helped bridge the gap between biochemistry and internal medicine. A large number of the many individuals who passed through Van Slyke’s laboratory went on to professorships of internal medicine or biochemistry or to other important posts in the US and abroad. Some of these were Vincent P. Dole, Franklin C. McLean, Christen Lundsgaard, John P. Peters, Michael Heidelberger, and A. Baird Hastings, who succeeded Folin in the chair of biochemistry at Harvard.

In 1914 the directors of the Journal of Biological Chemistry asked the Rockefeller Institute to take over its publication, with Van Slyke (age 31) to join the editorial board as managing editor. The nine-year-old Journal was the only publication in the US devoted solely to biochemistry. As such, it was to set the standards for publication of experimental data which would determine the direction and quality of biochemical research in this country. Toward the end of 1925 the ownership of the Journal and its management were transferred from the Rockefeller Institute to the American Society of Biological Chemists, and the editorial office was moved to Cornell University Medical College in New York City. Stanley R. Benedict (1884-1936) was appointed managing editor. Van Slyke, who remained on the editorial board until 1950, had also served as president of the society in 1921 and 1922.

Shortly after his retirement from the Rockefeller Institute in 1948, Van Slyke joined the newly formed Brookhaven National Laboratory of the Atomic Energy Commission in Upton, NY, as Assistant Director for Biology and Medicine. He remained at Brookhaven until his death at age 88.

Clinical chemists are especially indebted to Van Slyke for his collaboration with John P. Peters (1887-1955) of Yale University in the writing of the two-volume classic, Quantitative Clinical Chemistry (1931, 1932), which, for more than 30 years, was the authoritative source for clinical chemistry and even today re-
mains a valuable resource for the history of clinical chemical methods. A member of the National Academy of Sciences, Van Slyke was awarded the National Medal of Honor by President Lyndon B. Johnson in 1965.

REFERENCES AND NOTES

1. This article, being submitted on the occasion of the 50th anniversary of the American Association for Clinical Chemistry, is intended to inform the members of the ACS Division of History of Chemistry about the early foundations of this discipline.


10. G. S. Hall, "Laboratory of the McLean Hospital, Somerville, Mass.," Am. J. Insanity, 1895, 51, 358-364.


17. O. Folin, Ref. 3.


23. Ref. 18, p 19.


ABOUT THE AUTHOR

Ami Argand (1750-1803), during his short lifetime, contributed several innovations that would have a profound impact on future generations; yet his work is relegated to at best a footnote if mentioned at all. Argand’s most productive years coincided with the tumultuous decades of the Chemical Revolution. He was acquainted with many of the major protagonists on both sides of the debate concerning the new chemistry.

Argand was born in Geneva on July 5, 1750, the son of a watchmaker. His father was able to provide a university level education for his very talented son. At the University of Geneva Argand’s studies were directed by Horace Benedict de Saussure (1740-1799), an internationally known scholar who made significant contributions in the fields of natural history and physics (1). De Saussure had studied chemistry in Paris in 1768 and had kept up a relationship with many of the leading Parisian scientists. Thus it made it possible for his protégé to be admitted into Parisian scientific circles. Much of what is known about Argand comes from the correspondence he maintained with de Saussure and others throughout his life.

Arriving in Paris in 1774, Argand became immersed in the scientific life of the city. He became acquainted with Lavoisier who, although not involved in teaching as a profession, welcomed young students into his laboratory to assist him with his experiments. Argand’s first significant contribution was an improvement in the technique of distillation. It has been suggested that Argand may have become interested and learned the technical details of the process from his association with Lavoisier. In 1773 Lavoisier was commissioned by the Minister of Marine to investigate reports of a desalination plant for use on ships that had been demonstrated in London by a Portuguese scientist Jean de Magellan (1722-1790) (2). Lavoisier corresponded with Magellan and prepared a report in 1775 which also included further investigations he carried out himself. This report, Mémoire sur une Nouvelle Méthode Distillation appliquée à la distillation des Eau-de-vie-et a celle de l’Eau de Mer, dated July 1, 1775, also included a consideration of the problems associated with the distillation of spirits, a very important industry of the day. The major problem associated with the dis-
illation of spirits such as brandy was the slowness of the process with the equipment available at the time. By 1778, Argand developed an improved distillation technique by introducing a preheater step in the apparatus. The spirits to be distilled were used as the cooling fluid in the worm-cooler belonging to the still. Argand attempted to enter into an agreement with the Director General of Finances in Paris to give the government the rights to the process. In return Argand wanted a limited, though exclusive privilege to produce brandy and other spirits derived from wine. A test of the new distillation technique was deemed necessary before any decision could be made. After several years of delays it was decided that Argand’s apparatus would be tested by the Societe Royal des Sciences de Montpellier. Montpellier is in the region of France where the greatest production of wine was and still is taking place and thus was a suitable venue for the test. With his preheater Argand was able to distill almost twice the amount of spirits using less coal in about the same time as compared to conventional stills. The academicians reported to the Director General that the process was a significant improvement but in their opinion insufficient to warrant the monopoly that Argand had sought. “The success was so striking that his pre-heater was introduced in a period remarkably shorter than that of most other improvements of the distilling trade (3).”

Argand had impressed one of the most prominent members of the Montpellier academy, Philippe-Laurent de Joubert, who hired Argand and his brother Jean (1744-1834) to construct a distillery using his design on Joubert’s estate. The next several years were spent by Argand in the south of France in connection with the distillery and other projects. It was during this period that Argand realized the necessity for improved lighting in the distillery. As Argand stated in his 1785 monograph Decouverte des Lampes (4):

It was in 1780 that he produced the first one. Actively and continually occupied with a large distillery, which he had founded in Languedoc, it was sufficient at that time to produce a large amount of light in his factory. He delayed to quieter times the development of methods which were indicated by his theory, and the precision of the details, without which the major effect of these Lamps would have been missed. He made an addition to this first Lamp in 1782 during the Assembly of Estates of Languedoc. It commanded the attention of the most eminent and respectable people...it was at Montpellier that M. Argand produced his Lamps; which he proposed to improve more and more: that he kept it secret from the public as it should be (served), that is to say, in presenting to (the public) only complete instruments, and constructed with the precision which was practically impossible in the Provinces, and rare in the Capital, for new instruments. M. De Saint-Priest and M. De Joubert in particular were so struck by the increase in light produced by this Lamp, that they foresaw all the advantages which one could derive from it...

The construction of the lamp about 1780 was not an isolated technical feat, but represented the practical application of Argand’s theory of combustion, which he called his principle.

Argand and all his contemporaries were well versed in the phlogiston theory of combustion and the phlogiston nomenclature. His arrival in Paris in late 1774 coincided with the emergence of Lavoisier’s combustion theory (5). Lavoisier by 1775 had already demonstrated that when lead or tin was heated in a sealed container there was no change in weight. Opening the sealed vessel led to a rapid inrush of air and an increase in the weight of the system. The fateful dinner meeting with Joseph Priestly, hosted by Lavoisier, where he described his newly discovered dephlogisticated air, had already taken place in October, 1774. The Easter Memoir of 1775 “On the Nature of the Principle which Combines with Metals during Calcination and Increases Their Weight” had been writ-
Argand's concept of combustion was a mixture of old and new ideas. He believed that "inflammable air" (hydrogen) was responsible for combustion and not phlogiston. However, combustion required "dephlogisticated air" (oxygen) in order for burning to occur. The "dephlogisticated air" was destroyed, and the fire-producing material from the "inflammable air" formed the flame itself. Light was considered by Argand to be an element and was a byproduct of the flame that produced the illumination during combustion. The flame itself provided the heat produced in combustion.

The observation that combustion produced "fixed air" (carbon dioxide) and water as byproducts for organic fuels had to be explained. Argand rationalized this as the combination of part of the "dephlogisticated air" with material in the substance from which the "inflammable air" had been liberated. The key to the process was the amount of "dephlogisticated air" and its heating principle that mixed with the "inflammable air." At higher temperatures Argand believed that all the fuel would be converted to "inflammable air" and only would combine with the "dephlogisticated air" to produce water and a flame that would have great clarity and brilliance.

One of the major faults of Argand's principle was that he had never attempted to verify it experimentally. Because he was able to produce a lamp which was so far superior in its illuminating ability, he felt his theoretical framework was correct. Argand did not initially look at his invention in a commercial sense. Later when he did it was to cause him no end of trouble.

Argand went to England in 1783 and remained there working on his lamp enterprise until 1785. He became acquainted with Joseph Priestly and Richard Kerwin, the leading English supporters of the phlogiston theory. Because of his prolonged absence from France he was probably not fully informed of the definitive experiments and papers being presented by Lavoisier in support of the oxygen theory of combustion and acidity.

One of the major problems with the new theory of Lavoisier was the combustion of hydrogen and the water question. In 1783 Argand had noticed the formation of water during combustion. His lamp when designed with an attached chimney, allowed for the condensation of water which ordinarily would have been lost. However his interpretation of this observation was along the lines of that of his English colleagues. Indeed, Argand had used his lamp as a means to demonstrate to his English colleagues the validity of his combustion principle. Cavendish had explained the formation of water as the combination of two gases which he assumed were really water with or without phlogiston. Combustion released the phlogiston and hence water would result. Lavoisier in that same year reported the experiments he had performed in collaboration with Pierre Simon de Laplace on the combination of oxygen and hydrogen in the presence of an electrical spark. His interpretation of the formation of water as a compound was the proverbial final nail in the coffin of the phlogiston theory. By 1786, Argand had returned to Paris because of his lamp business; after long discussions with Claude-Louis Berthollet (1748-1822), he became a convert to the oxygen theory. Argand lost further interest in his lamp except for the commercial aspects of the invention.

There seem to have been two periods involved in the construction of the Argand lamp: 1780-82, when the basic model was produced; and 1783-84, when certain improvements were made. These improvements were the addition of a wick-raising mechanism and the chimney. The first technical description of the lamp appeared in a paper by the Comte de Milly in 1784 in Observations sur la physique:

To construct a lamp on these principles it is necessary only to have two cylinders of the same length, but different diameters, one of which enters into the other, leaving between them a space in proportion to the effect you want. These two cylinders are placed vertically and parallel to each other, and are soldered to a common base, leaving the inner cylinder hollow and open from one end to the other. The hollow space between the cylinders, which is closed at the base and open at the top, serves to contain the oil that feeds the flame. You fashion a circular wick with cotton cloth, which will enter, in a circular manner, the space between the cylinders. This wick will roll along on a circle of tin-plate or copper placed in the space between the cylinders, which is filled with oil. If you light the wick with everything set up in this way, the hollow cylinder which is open from one end to the other, will act as a pipe conducting air which will be rarefied by the flame of the wick. Thus, the flame will be animated by both the interior and exterior air, and the size of the flame and the intensity of the heat will be prodigiously increased.

Milly adds in his description how he came to write about the lamp as follows (6):
This ingenious lamp was, as I have said, invented by M. Argand, a skillful chemist of Geneva. Monsieur Fanjas De Saint Fond, to whom Monsieur Argand had shown the mechanism and from whom I received these details, decided to communicate them to me only with the intention of preserving for the author the merit of its discovery, which has been disputed by people who have wanted to copy it.

Argand was to spend a good part of the rest of his life in litigation against all those who copied it in France and England, trying to obtain what should have been the rewards for his creativity. This endless round of court battles as well as the Revolution of 1789 exacted a major toll on Argand's health and wealth and thus his ability to focus on new projects.

While working for Joubert, Argand became acquainted with the Montgolfier brothers, Etienne (1740-1810) and Joseph (1745-1799). The Montgolfiers are generally credited with the birth of aviation. On the fifth of June, 1783 they launched the first successful hot-air balloon at Annonay, a small city near Lyon. Argand's friendship and collaboration with the brothers would continue throughout most of the rest of his life. An invitation from the Academie des Sciences brought the brothers and Argand to Paris that summer of 1783. A demonstration of the balloon was performed at Versailles on September 19, 1783 for Louis XVI and his court. Argand's contribution to this venture seemed to be to help in the preparation and launching of the balloon. For the balloon launched in March, 1784 he did contribute a version of his chimney lamp which had been modified by Joseph Montgolfier. This allowed the construction of a balloon with a very small aperture to heat the air in the balloon. "Its fuel was a three-to-one mixture of olive oil and grain alcohol impregnating a circular wick of spun cotton. The principle was that convection draft, air for combustion being carried up through the center of the wick by an iron tube that acted as a blower."

Shortly thereafter Argand went to England with the intention of demonstrating his lamp. He reported to Etienne Montgolfier on November 21, 1783 that the English were immensely jealous of his accomplishment. A friendship began in London with the Swiss-born physicist Jean-André de Luc (1727-1817), who was a tutor to the family of George III. This led to an invitation to demonstrate the balloon and the lamp at Windsor. On the 25th of November, 1783 Argand launched a small balloon, to the amazement of George III, while at the same time demonstrating the superior illumination of his lamp. Coincidentally in Paris on the same day, the first manned journey in a free balloon by Pilatre de Rozier and the Marquis d'Arlande took place. Argand was urged by de Luc to obtain a British patent for his invention. Patent number 1425 entitled "Lamp Argand's Specification" was issued to Argand and published on July 3, 1784. In this patent Argand states:

...that I had, after much trouble and considerable expense, found out and invented A LAMP THAT IS SO CONSTRUCTED TO PRODUCE NEITHER SMOKE NOR SMELL, AND TO GIVE CONSIDERABLY MORE LIGHT THAN ANY LAMP HITHERTO KNOWN.

Having secured this patent, Argand, with an eye to its commercial possibilities, entered into a partnership with the firm of Matthew Boulton of Birmingham to manufacture the lamp. Matthew Boulton (1728-1809) and James Watt (1736-1819) were partners in several ventures and were part of the famous Lunar Society. It was at the Lunar Society in Birmingham that Argand met many of the defenders of the phlogiston theory.

The time Argand spent in England was the high point of his life. Called back to Paris in 1786 to deal with the numerous cases involving the piracy of his lamp and the claims as to whether he was the inventor of the lamp, Argand suffered both a physical and financial breakdown. Even though he was able to establish a factory at Versoix near Geneva, the French Revolution was the final blow to Argand as he lost most of his assets. The invention of the lamp was one of the major reasons that a search began in the 1840s for better fuels than the naturally occurring whale oil. This would ultimately lead to the discovery of coal oil (kerosene) and the beginning in earnest of the hydrocarbon age.
ACKNOWLEDGMENT

I wish to express my sincerest appreciation to Dr. W. A. Smeaton, Reader Emeritus in the History of Science, University College, London, for his help and advice in the preparation of this paper.

REFERENCES AND NOTES

*A version of this paper was first presented at the 213th American Chemical Society Meeting, San Francisco, CA, April, 1997, HIST 006.


4. F.A. Argand, *Decouverte des Lampes*, Geneve, 1785. The full text of this work can be found in Ref. 11.


7. Fanjas de Saint Fond was involved in the early work on lighter-than-air-balloons in 1783-84 and wrote one of the first books about ballooning.


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THE ART OF DISTILLATION AND THE
DAWN OF THE HYDROCARBON SOCIETY

Martin D. Saltzman, Providence College

Of all the techniques employed in the laboratory none has such an ancient lineage as that of distillation. The first uses of distillation are shrouded in antiquity, but certainly by the Middle Ages a body of literature existed describing various aspects of the technique. The Encyclopedia of Denis Diderot (1713-1784), which appeared in seventeen volumes from 1751-1772, contains an extensive entry on distillation with many references to various treatises on the subject. R. J. Forbes has produced perhaps the most definitive study of the subject from antiquity through the nineteenth century in his book A Short History of the Art of Distillation (1).

The product that most immediately comes to mind that is associated with distillation is alcohol. However, another product, petroleum, has had far greater consequences for our society. The beginning of the hydrocarbon society (2) is usually associated with the well drilled at Titusville, Pennsylvania, by Edwin L. Drake (1819-1880) on behalf of the Seneca Oil Company. This well first produced crude oil on August 27, 1859, and thus the oil industry began as we know it today. Ida Tarbell has written, however (3):

...The development of the American oil industry does not begin, as is commonly said, with the discovery of oil in August, 1859, near Titusville, Pennsylvania. Dating a discovery, like dating the beginning of a war or a revolution, is one of history's most misleading short cuts. Discoveries like wars and revolutions have long backgrounds.

The roots of the oil industry can be traced back to the fourth century B.C. in the Middle East. In Mesopotamia, petroleum products were available from bitumen seeps, oil springs, and oil-bearing rock. Bitumen was used by the Sumerians, Assyrians, and Babylonians as caulking for their boats, irrigation systems,
and in making bricks. The Egyptians used bitumen in their mummification procedures. The material was obtained from the Dead Sea where huge balls periodically rise to the surface. The Egyptian trade was controlled by Arabs who gave the Arabic name "naft" to this product, from which is derived the modern term naphtha. Naft became a fearsome weapon in the arsenals of the Byzantine and Muslim armies and navies, which were contending for dominance in this region in the 7th century. It is believed that the weapon which became known as the "Greek Fire" may have been a distillate rather than crude oil. The weapon was used with great effect by the Byzantines at the Battle of Kyzikos in 680 BC in which the Muslim fleet suffered enormous casualties from burning.

The first recorded reference to distillation of crude oil appears in the writings of Muhammad al-Razi (1149-1210), a Persian physician and chemist, in his Book of Secrets. The process described involves the device called an al-imbig, which has been transliterated into English as alembic. The alembic became a standard piece of apparatus throughout the Middle East and Europe for simple distillation (Fig. 2). The distillate al-Razi described seems to resemble kerosene, that fraction of crude oil used for heating and lighting and the impetus for drilling the first oil well. A later reference to the distillation of crude oil is found in the writings of Hassan Al-Dimashki (1310-1370), a Syrian historian and man of letters (4):

Many types of naft are water white by nature and so volatile that they cannot be stored in open vessels. Others are obtained from a kind of pitch in a turbid and dark condition, but by further treatment they can be made clear and white by distilling them like rose water.

There are many reports in the Arabic literature of the medicinal value of naft as a curative for various illnesses. Crude oil was continually refined in the Middle East, particularly in the region surrounding the city of Baku in present day Azerbaijan from the seventh century AD onward.

Petroleum seeps in the United States had been discovered as early as 1627 in western New York near the present town of Cuba. The best sites were found in western Pennsylvania along a stream appropriately named Oil Creek, near the town of Titusville. These oil seeps were discovered by a Moravian missionary, David Zeisberger, in 1768. The Senecas had been using crude oil for medicinal purposes, and it soon became an item of trade with the European settlers. Physicians routinely prescribed crude oil in the first part of the nineteenth century as a cure for a variety of illnesses.

There were two major problems in the use of petroleum for lighting and heating. First, there was not an efficient burner for this material; and second, a supply of refined product was not available at a cost competitive with the other fuels available. In 1780 Francois-Pierre Ami Argand (1750-1803) invented a burner that produced an intensity of light that had never been possible before (5). The Argand burner was too expensive to produce for the mass market, but the development in the early 1850s in Austria of a burner with a flat wick which was much cheaper to produce solved the first problem. The flat wick became the standard in kerosene lamps and lanterns from that time onward and is still produced today in much the same way.

In 1850 one had the choice of a variety of liquid fuels of varying lighting ability and price. The best was sperm oil, but the American whaling industry had so decimated the sperm whale population that the cost of this product became prohibitive for the general population. Rosin oil, burning fluid, and camphene then became the principal fuels. Camphene, a mixture of purified turpentine and alcohol, was very popular even though it was particularly dangerous because of the volatility of its components and required a special burner. A
much better fuel was needed; and this was produced by Abraham Gesner (1797-1864), a Canadian physician by training but also a geologist, chemist, and inventor (6). Sometime in 1845 Gesner began experiments to produce a better fuel by dry distillation from a black mineral named albertite found in New Brunswick. He obtained a liquid whose use as a fuel for lighting he demonstrated as early as 1846 in public lectures on Prince Edward Island.

A similar material could be obtained by distillation of pitch found on the island of Trinidad (Fig. 3) and also of certain types of English fuel called cannel coal. In 1853 Gesner moved to New York to superintend the construction of the first commercial plant to produce this new hydrocarbon fuel, generically named rock oil. Gesner’s patent (US Patent 70525, Jan. 29, 1850) covered a process to produce a volatile fraction to which he gave the name keroselain, from the Greek keros for wax and elain for oil. For public relations reasons the name was changed to kerosene so that it resembled the name camphene. Kerosene was shown to be a much better value for money than any other of its competitors. This even included coal gas, both in terms of the cost and the resulting brilliance of the illumination. Kerosene became an instant success; by 1859 between fifty and sixty plants, representing an investment of four million dollars, had been built. These were based on Gesner’s process as well as a similar one that had been invented and patented by the Scotsman James Young (1811-1883) in Britain and the United States (US Patent 8833, March 21, 1852) (7). No one, however, at this time was producing kerosene in any significant quantities because of the lack of a supply of crude oil.

In parts of Pennsylvania wells had been drilled for some time which produced salt water as a source of salt. In many of these wells besides the salt water quantities of crude oil came to the surface. In 1849 Samuel Kier (1813-1874) conceived the idea of selling oil from the salt wells for medicinal purposes; but “Kier’s Petroleum or Rock Oil,” put up in half-pint bottles, was not a commercial success (Fig. 4). Having an excess of crude oil in his possession, Kier turned his attention to its use as an illuminant. Crude oil itself was unsatisfactory because of its odor and the smoke it produced when burned. Kier sought the advice of James C. Booth (1810-1888), a consulting chemist in Philadelphia, who suggested he distill the crude. A small-scale refinery was built in Pitts­burgh in 1850; and Kier’s product, which he named “car­bon oil,” was a local success. That prompted this pio­
Francis B. Brewer

ner in the family business. Brewer, Watson, and Company used the crude oil collected from trenches as both a lubricant and for lighting in the saw mill. Dr. Brewer was fascinated by the prospect of the commercial value of oil and persuaded his partners to try to develop this product.

In the fall of 1853 Brewer visited his alma mater with a sample of the rock oil that had been collected from the oil springs on the Brewer property. This was shown to Dr. Dixi Crosby of the Medical School and Professor O. P. Hubbard, a chemistry professor, and left for their evaluation. Hubbard believed the material to be potentially very valuable, but the limited supply made its prospects dim. Skimming the oil could at best produce eighteen gallons per day from the Brewer lands. By sheer coincidence in the fall of 1853, a few weeks after Brewer’s visit to Dartmouth, George Henry Bissell (1821-1884) (Fig. 5), a native of Hanover and an 1845 graduate of Dartmouth, happened to be visiting his birthplace. Bissell had been recently admitted to the bar in New York after a varied career which included serving as superintendent of public schools in New Orleans before becoming a lawyer. Bissell and his law partner Jonathan G. Eveleth were active promoters for the sale of the shares in newly formed companies. Bissell, by chance happened to see the bottle of rock oil in Crosby’s office and asked about it. Crosby related to Bissell that he had done a few simple experiments and was convinced this material could be a superior illuminant. Bissell recognized the connection between Brewer’s rock oil and Gesner’s coal oil now coming into general use. Ever on the lookout for a profitable venture, Bissell commissioned Dixi Crosby’s son Albert to go to Titusville in the summer of 1854 to obtain first-hand information and to evaluate the oil springs. The younger Crosby was impressed by what he saw, and Bissell and Eveleth began a plan to establish a joint stock company to purchase the oil-bearing properties in Titusville and to bring the product to market. In September, 1854 the Pennsylvania Rock Oil Company was founded with offices at 346 Broadway in the D. Appleton and Company building in New York. Brewer, acting on behalf of his partners, came to New York in the fall of 1854 to sign the papers at the offices of Bissell and Eveleth; and the company was officially incorporated in New York on December 30, 1854. In conversations with Brewer it became evident that Crosby had exaggerated greatly the quantity of oil present. Bissell and Eveleth became somewhat skeptical and hesitant about proceeding. However, Brewer proposed an offer to Bissell and Eveleth they could not refuse. Either Bissell or Eveleth could personally inspect the property, and if they were not satisfied, the agreement would be canceled; and Brewer, Watson and Company would pay all the expenses so far incurred. Before either of them could go to Titusville, a letter arrived from New Haven. Anson Sheldon, a retired minister who had heard about the new venture, suggested that Bissell and Eveleth should visit New Haven, as there were parties who might be interested in

George M. Bissell
investing in their company. One of these was James M. Townsend, president of the City Savings Bank. Townsend and his partners, however, specified two conditions before any shares would be bought: a visit to the property by a representative of their group, and a scientific analysis to determine the commercial value of petroleum. Thus the rationale for one of the most important landmark analyses by distillation came about. Two men were chosen for this enterprise, Luther Atwood of Boston and Benjamin Silliman, Jr., of Yale College. On November 4, 1854 Eveleth and Bissell wrote to Frank Brewer the following (8):

Dr. Atwood of Boston is analyzing the oil, and it is in the hands of Prof. Silliman of Yale College. We shall have it analyzed by several of the best chemists in the country, and shall make use of their analysis and get some of your best western men to examine and to testify as to facts there.

Luther Atwood (1826-1868) was a partner with his brother William and Samuel Philbrick in 1854 in the US Manufacturing Company in Waltham, Massachusetts in 1854 (9). This company had been organized to exploit a patent of Luther Atwood to make a lubricant for machinery by the distillation of the coal tar residues produced by gas works (US Patent 9,630 March 29, 1853). Atwood in 1856 established the coal oil business in Boston and succeeded Abraham Gesner as chief chemist of the Kerosene Company in New York. Atwood seems to have given the Brewer oil sample a fairly cursory examination and pronounced it to have potential as an illuminant.

Benjamin Silliman, Jr. (1816-1885) was the son of Benjamin Silliman (1779-1864), professor of chemistry at Yale College (10). Silliman, Jr. had studied with his father at Yale, where he received his undergraduate degree in 1837 and an MA in 1840. After a short period spent in Boston with the chemist Charles T. Jackson, Silliman returned to New Haven and acted as a laboratory instructor for his father's advanced students. In 1846 the Yale Corporation created a professorship in applied chemistry to which Silliman Jr. was appointed. Because the position had no salary attached to it, Silliman was forced to leave Yale and went to the University of Louisville. In 1854, with the retirement of his father, he assumed the latter's position; and it was in this year he was approached to analyze the oil sample provided by Brewer. It seemed logical to the New Haven investors that a chemist of Silliman's stature should analyze the oil. His was a very thorough analysis; and it was his report, dated April 16, 1855, that was the key in getting Sheldon's group to back the oil venture. Silliman wrote to Eveleth and Bissell on December 21, 1854 the following, which was relayed to Frank Brewer (11):

I am very much interested in this research and think I can promise you that the results will meet your expectations of the value of this material for many most useful purposes. The oils which I have so far obtained are perfectly fluid...As yet the quantities I have obtained have all been distilled in glass from an original weighted quantity, and the weights of the several products have been carefully noted. That operation has consumed from 2 to 3 weeks and is still in process.

Silliman reported further progress which was passed on by Eveleth and Bissell to Brewer (11):

Since the above letter was written from which the extract has been taken, the analysis has been extended and six different oils produced, making in all that has thus far been obtained 50 per cent...the Professor is of the opinion that the yield will be at least 75 or 80 per cent of pure oil.

On February 17, 1855 Eveleth reported to Brewer (11):

Silliman is progressing with the analysis, we have been obliged to get all new apparatus for him, they had an explosion, but we hope to have the report soon.

This was followed on April 10, 1855 by a letter from Anson Sheldon to Brewer with further news of Silliman's work (11):

Professor Silliman has not yet completed his photometrical examination of the Rock Oil in comparison with other burning fluids, but will probably wind up his analysis in all this week....The value of the oil depends mostly on its properties as a burning fluid. In this respect the analysis and its results, has [sic] been highly satisfactory.

On April 21, 1855 Eveleth wrote to Brewer (11):

Have rec'd. Prof. Silliman's Report. Bill is $526.08. We had paid out for other things for him, over $100. Could not have the report till paid for....It is now in the hands of the Printer. Will be ready for middle of next week....It is a great report.

Anson Sheldon wrote to Brewer about the report on April 23, 1855 (11):

Silliman's Report is now in my hands, and is favorable to our enterprise, but as Bissell and Eveleth had failed to meet the Professor's wishes in placing $100 to his credit in the Bank of New York...he placed the Report in the hands of a friend in New York with instructions not to deliver it up until satisfactory arrangements were made for the payment of his bill which amounts, (including the expense of his appa-
ratus employed in the analysis), to the round sum of $526.08 about $75 had been previously paid...making the whole expense exceed $600. This sum may at first appear exorbitant, but when we take into account the time consumed, the nature of the experiments, and the value of the Report, I think those concerned will be satisfied...Several gentlemen here of known ability have assured me that they should take some stock, if Silliman's Report should be favorable to the oil. That point is settled, the Report is more favorable, even, than I had dared to hope.

Anson Sheldon reported to Frank Brewer on May 11, 1855 that "Prof. Silliman proposes to take some stock (11)." The report, printed in New Haven, amounted to twenty 5" x 8" pages.

How did Silliman do this most important analysis? His own words provide the answer (12):

To determine what products might be obtained in the oil, a portion was submitted to fractional distillation.* *(Fractional distillation is a process intended to separate various products in a mixture, and having unlike boiling points, by keeping the mixture contained in an alembic at regulated successive stages of temperature as long as there is any distillate at a given point, and then raising the heat to another degree, etc.).

From a sample of 304 grams of crude, Silliman was able to distill 160 grams into several different fractions (12):

We infer from them (boiling points) that the Rock Oil is a mixture of numerous compounds, all having the same chemical constitution, but differing in density and boiling points, and capable of separation from each other, by well-regulated heat.

Silliman performed various chemical tests such as elemental analysis, tests for acidity and corrosive action on copper, inertness to hydrochloric, chromic, and acetic acid, as well as the action of metal oxides. Lack of reaction with calcium chloride, potash, sodium carbonate, and calcium oxide was also observed. Reaction with bleaching powder produced a product resembling in character that of chloroform. The oil was slightly soluble in alcohol but easily soluble in ether. Silliman did a second distillation of the crude oil, this time on a much larger scale and with a copper still. The temperature was raised to 280°C initially and then to 300°C. In this narrow range over 43% of the crude oil distilled. The temperature was raised again, this time to above 360°C, and another 31% of the crude distilled. This fraction, after treatment by boiling with water, was used as the material for the illumination tests. Thus close to 75% of the crude oil was separable into distillates by using external temperatures ranging from 280-360°C. Further distillation at even higher temperature in the end led to a recovery close to 90%. Silliman concluded (12):

The Drake Well in 1866. Peter Wilson and E. L. Drake are shown standing in the foreground.

It is safe to add that, by the original distillation about 50 per cent of the crude oil is obtained in a state fit for use as an illuminant without further preparation than simple clarification by boiling a short time with fair water.
The report concluded with a discussion of the naphtha as an illuminant and photometric studies. Silliman stated that the fraction from the high-temperature distillation, that which boiled below 360°C, burned without smoking and gave a light which was (12):

.....pure and white without odor. Its rate of consumption was one-half of those of most oils such as camphene which was in common use. I have submitted the lamp burning Petroleum to the inspection of the most experienced lampists who were accessible to me, and their testimony was, that a lamp burning this fluid gave as much light as any which they had seen, that the oil was spent more economically, and the uniformity of light was greater than in camphene.

To test the intensity of the light Silliman constructed a photometer. The standard used was Judd’s Patent Sixes Sperm Candles which were assigned a value of 1. Compared to coal gas light, sperm oil, and camphene, the Rock Oil produced the highest value for the light intensity and possibly the best value for cost. At this time it was difficult to fix a value for the Rock Oil because it was not yet in commercial production. Silliman noted that preliminary results indicated the oil was also a good lubricant (12):

In conclusion, gentlemen, it appears to me that there is much ground for encouragement in the belief that your Company have in their possession a raw material from which, by simple and not expensive process, they may manufacture very valuable products. It is worthy of note that my experiments prove that nearly the whole of the raw product may be manufactured without waste, and this solely by a well directed process which is in practice, one of the most simple of all chemical processes.

The report created considerable interest in New York and New Haven, and two-thirds of the shares were sold reasonably quickly. For legal reasons the Pennsylvania Rock Oil Company of New York was reincorporated in Connecticut on June 25, 1855, with offices in New Haven and Benjamin Silliman (13) as president.

All did not go smoothly with the attempts to obtain oil in commercial quantities. The method of surface collection was abandoned in favor of the novel approach of drilling a well. Edward Drake (14) was hired in December, 1857 by the New Haven group to act as superintendent at the Oil Creek site and to begin the drilling. Various delays postponed drilling until May, 1859; and there was little confidence that drilling for oil in solid rock would ever amount to anything. The shareholders became increasingly disenchanted, and the money raised by the stock offering was running out. Frank Brewer traded his shares for cigars, which he gave out freely to young men in Titusville. What a mistake he had made became very evident on the weekend of August 27, 1859, when the first oil came in. Although Drake is usually given most of the credit for the dawn of the hydrocarbon society, would it have started in 1859 if not for Benjamin Silliman, Jr. and his application of the art of distillation?

ACKNOWLEDGMENT

I would like to thank the Drake Well Museum and the Pennsylvania Historical and Museum Commission for assistance in obtaining copies of the Brewer papers. A special note of appreciation goes to my colleague Mario DiNunzio of the History Department of Providence College for his help in preparing this paper.

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2. The term hydrocarbon society has been used by Daniel Yergen in his book The Prize, The Epic Quest for Oil, Money & Power, Touchstone, New York, 1991.
4. Ref. 1, p 53.
7. For further information about James Young, see J. Butt, “Legends of the Coal Oil Industry (1847-64),” Explorations in Entrepreneurial History, 1964, 2, 16-30.
8. Letter obtained from the Brewer Archives at the Drake Well Museum, Titusville, PA.
12. B. Silliman, Jr., Report on the Rock Oil, or Petroleum from Venango Co., Pennsylvania, J. H., Benham’s Steam Power Press, New Haven, CT, 1855 (I would like thank
Dr. F. L. Holmes for his assistance in obtaining a copy of this report.)


14. Edward L. Drake was by trade a railroad conductor on the New York & New Haven Railroad. Forced by ill health to retire, he retained a pass for free travel. For this reason he was hired by Eveleth and Bissell in 1857 to go to Titusville to obtain some legal papers. He was introduced as "Colonel" to impress the locals and forever has been known as such. He studied the salt well drilling operations near Syracuse and Pittsburgh on his trip and became convinced that this was the best way to extract the petroleum. His persistence in drilling led to the birth of the oil industry in Pennsylvania. Although not trained as an engineer, Drake was the inventor of the idea of using pipe to prevent the filling of the hole driven in the bed rock by sand and clay.

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1999 DEXTER AWARD

The Dexter Prize Committee of HIST has selected Dr. Mary Jo Nye, the Thomas Hart and Mary Jones Horning Professor of the Humanities and Professor of History at Oregon State University, as recipient of the 1999 Dexter Award for Outstanding Achievement in the History of Chemistry. Professor Nye is the author of four books and more than three dozen articles on the history of chemistry and its interactions with physics. For 25 years she participated actively in the formation of leading undergraduate and graduate programs in history of science at the University of Oklahoma, and she served for three years as President of the History of Science Society. The award will be presented at a luncheon at the conclusion of the Dexter Award Symposium at the 219th National American Chemical Society meeting in the spring, 2000, in San Francisco.
NAPOLEON BONAPARTE, FRENCH SCIENTISTS, CHEMICAL EQUILIBRIUM, AND MASS ACTION

Sol W. Weller, SUNY at Buffalo

**Introduction**

This paper involves two intertwined themes. One is the relation of Napoleon Bonaparte (1769-1821) with leading French scientists of his time. The second is the beginning of two concepts important in chemistry: (a) reaction reversibility and chemical equilibrium, and (b) the role of relative masses of reactants and products in determining the position of equilibrium. These ideas are now taken as axiomatic, but they were introduced into chemistry only 200 years ago by the French chemist Claude Louis Berthollet (1748-1822), a friend and confidant of Napoleon.

The period from roughly 1750 to 1830 was a brilliant one for mathematics and chemistry in France. The mathematicians Joseph Louis Lagrange (1736-1813), Gaspard Monge (1746-1818), Pierre Simon Laplace (1749-1827), Adrien-Marie Legendre (1752-1833), and Joseph Fourier (1769-1830), and the chemists Antoine Lavoisier (1743-1794), and the chemists Antoine Lavoisier (1743-1794) and Claude Berthollet flourished during this period. A portion of this era, 1795-1815, describes the Napoleonic age, a time when Napoleon exercised power in France. What was the influence of Napoleon on the personal and scientific careers of these savants?

**Some Historical Background**

**Berthollet:** Modern chemistry developed rapidly during the latter half of the 18th century. Discovery of elements; development of a rational nomenclature for the naming of elements and compounds; determination of the constitution of air and water; and the explication of combustion occurred during this period. Lavoisier was the leading French chemist until he was beheaded in 1794. After Lavoisier, Berthollet was one of the most distinguished of the French chemists. Among other things, he had determined the composition of ammonia in 1785, prussic acid in 1787, and hydrogen sulfide in 1789. Berthollet pointed out that the absence of oxygen in HCN and H₂S disproved Lavoisier's hypothesis that all acids contain oxygen. As director of the Gobelins dye works, Berthollet studied the preparation of pigments and dyes. He discovered potassium chlorate and its explosive properties in 1788, and in 1785 he established the utility of chlorine and hypochlorites as bleaching agents (1,2). [As a matter of principle, Berthollet refused to file patents or make a profit from his work on bleach.] During the French Revolution Berthollet served as commissioner of the national mint and as commissioner of agriculture. Berthollet was the first French scientist to support Lavoisier's theory of combustion in 1785, and he helped to popularize Lavoisier's new system of chemical nomenclature.

**Monge:** Gaspard Monge, a good friend of Berthollet, was a mathematician and founder of descriptive geometry, engineer (author of The Art of Making Cannon), and public servant on the national stage (3). Monge also had connections with Lavoisier. In 1783 he proved the nonelementary nature of water by exploding...
a mixture of hydrogen and oxygen with an electric spark and showing that water was the reaction product. Monge became the intermediary for the meeting of Berthollet with Napoleon and the subsequent friendship between chemist and general. The circumstances were unusual. As Minister for the Navy and the Colonies during 1792-93, Monge had occasion to welcome Napoleon in that capacity. Napoleon reminded Monge of this in his cordial letter to Monge in 1794. They met, liked each other, and became friends for life. Berthollet met Napoleon through Monge. Throughout the years, Monge and Berthollet were Napoleon’s favorites among all the scientists.

**Laplace:** Laplace, mathematician and mathematical astronomer, also was associated with Lavoisier—surprisingly, as an experimentalist. Laplace was already at work on his *Celestial Mechanics* when he was recruited by Lavoisier in 1777 to help in planning and carrying out experiments on the effects of heat on various substances. They devised the first ice calorimeter, designed by Laplace, in order to measure heats of combustion, specific heats, and the “animal heat” generated by the respiration of a confined guinea pig. The Lavoisier-Laplace Mémoire sur la Chaleur was published by the Royal Printing Office in 1783 (4). The early work of Laplace on the stability of the solar system (1773) had earned him associate membership in the Academy of Sciences; he was promoted to full membership in 1785, the same year in which he, as professor of mathematics in the École Militaire, was an examiner of Napoleon when the 15-year old entered the school.

**Fourier:** Fourier, orphaned at age 8, chose mathematics over priesthood as a profession. When the short-lived École Normale was created in 1794, Fourier became chair of mathematics, and he became a professor in the successor institution École Polytechnique. Fourier was recruited by Berthollet to participate in Napoleon’s 1798 expedition to Egypt. He was made secretary of the Institut d’Égypte when it was established by Napoleon in 1798.

**Napoleon:** Napoleon’s meteoric rise to power is well known. He was commissioned as a 2nd lieutenant in the artillery at age 16, appointed captain at age 23, brigadier general at 25, commander of the Army of Italy at 26, and First Consul at 30. He crowned himself emperor at age 35. Less well known are Napoleon’s special interest and ability in mathematics, already evident during his teenage years (5,6). His continuing interest in mathematics and applied science may partially explain the closeness that developed between Napoleon, Monge, and Berthollet in later years. Other factors were their mutual respect and the fact that as trusted advisors, Monge and Berthollet were nonthreatening to Napoleon as competitors for power.

**Napoleon’s Italian Campaign**

An early sign of the special regard in which Napoleon held Monge and Berthollet is their selection, by the Directoire, at Napoleon’s recommendation, to visit Italy in 1796 as members of a six-person “Governmental Commission for the Research of Artistic and Scientific Objects in Conquered Countries.” Their assignment was to choose and send back to Paris valuable objects of art and church treasures. Monge informed his wife that 300 crates were needed to convey to France the objects taken from Italy; the Mona Lisa was included. Berthollet, born in Savoy, spoke Italian as well as French. He was also an early writer on techniques for restoring fine art; in one of his reports from Italy he discussed means of restoring several paintings of Raphael.

**Napoleon’s Campaign in Egypt**

After a proposed invasion of England was canceled, in 1798 Napoleon undertook a campaign in Egypt (7). Napoleon asked Berthollet to organize a “Committee on the Arts and Sciences” to accompany the army. Among the recruits were Monge, Fourier, the zoologist
Étienne St. Hilaire (1772-1844), Nicolas-Jacques Conté (1755-1805, inventor of the graphite pencil and the Conté crayon), the mineralogist Déodat de Dolomieu (1750-1801, whose name is given to the Dolomites in the Alps and to the mineral dolomite), and the physicist Étienne Malus (1775-1812), discoverer of the polarization of light by reflection.

In Egypt Napoleon established the Institut d’Egypte, modeled after the French institution. He named Monge as its first president and himself as vice-president. Berthollet succeeded Monge as the second president. After initial military successes, things went poorly for Napoleon in Egypt, and he decided to make a sudden and secret return to France in 1799. Of the scientists, Napoleon chose only Monge and Berthollet to accompany him on the dangerous voyage back. Both Monge and Berthollet were later cited, by Napoleon and by his chief-of-staff, General Berthier, for bravery in Egypt.

**Honors, Appointments**

After the Egyptian campaign, Napoleon showered titles and well-paying positions on many of the scientists who had been participants in Egypt — and on many who had not. The list is long. In 1802 Napoleon created the Order of the Legion of Honor; Lagrange and Laplace were made Grand Officers of the Legion of Honor. Berthollet, Laplace, Lagrange, and Monge were made Counts and were named to the French Senate. Senators were appointed for life, at an annual salary of 25,000 francs. In 1803 Napoleon established a system of “Senatoriates” (or “superprefect” positions) in which France was divided into 15 districts for legal appeals. Monge and Berthollet were two of only three scientists selected for these positions. Appointment to a Senatoriate entailed an additional annual revenue of 20,000-25,000 francs, along with a residential palace in an urban seat.

When Fourier returned to France from Egypt in 1801, he was appointed by Napoleon as prefect of the Department of Isère, headquartered in Grenoble. His administration there was outstanding during a 12-year tenure, and Napoleon made him a Baron in 1808. Although Fourier had difficulty in surviving Napoleon’s downfall, he was finally appointed Director of the Statistical Bureau of the Seine and elected to the Académie des Sciences, the Académie de Medicine, and the Académie Française.

Laplace was named Minister of the Interior by Napoleon, but he was a poor administrator and was replaced by Napoleon after only six weeks in office. Laplace successfully shifted loyalty under numerous changes in regime. After the Bourbon restoration, Louis XVIII raised him to the peerage as the Marquis de Laplace.

**What Did the Scientists Gain from Their Interaction with Napoleon?**

Why did Napoleon bestow honors and high positions on the scientists? Were Napoleon’s thoughts and actions influenced by the scientists? In a long-term sense, the answer is probably not. However, the work of the scientists on short-term, utilitarian problems was probably useful to the general. Napoleon always emphasized the utility of science and technology to improve the quality of life and to increase the economic status of the French people. The physical circumstances of the scientists were influenced, of course, by Napoleon’s predilection to favor scholarly scientific prominence. The personal lives of the scientists were greatly affected by the rewards of titles and well-paying positions bestowed by Napoleon. When Berthollet managed to fall into debt in 1807, Napoleon sent him 150,000 francs to clear his record.

A more difficult question is: To what extent were the professional activities of the scientists changed by their association with Napoleon? In most cases the answer is, not very much. Laplace, for instance, proceeded with his investigations of celestial mechanics and produced a five-volume treatise plus a summary volume, along with a two-volume work on the mathematics of probability.

In a few cases the circumstances of Napoleonic interaction led to new features of intellectual life for the scientists. Fourier is one example. While in Egypt as a participant in Napoleon’s venture there, Fourier had suggested that a record of French discoveries in Egypt be prepared. As a result, Fourier had a major role in writing the 21 volumes of the *Description de l’Egypte*, which appeared between 1809 and 1828. Fourier can be remembered as an early Egyptologist as well as a major figure in mathematical analysis. The influence of Napoleon on the professional career of Berthollet is considered in the following section.

**Elective Affinity, Chemical Equilibrium, Mass Action**

**Elective Affinity:** The question, “Why do chemicals react?” has been an enduring one. One prominent an-
swum during the nineteenth century was, "Because they have an affinity for each other." Elaborated theories of chemical affinity were proposed. The Swedish chemist Torbern Bergman (1735-1784), among others, published tables in which substances were ranked according to the intensity of their affinity. Substances of greater affinity were considered capable of displacing others with lesser affinity. If two substances combined, they were thought to have a selective or "elective" affinity for each other. Moreover, if a reaction proceeded, it went to completion (8,9). The ideas of equilibrium in a chemical reaction and the role of reactant mass became of general interest only after Berthollet's visit to the Egyptian "Natron Lakes" in 1798.

**The Natron Lakes:** In Egypt Napoleon gave Berthollet various practical assignments. These included finding fuels for bread ovens, substitutes for hops in the brewing of beer, and raw materials for the manufacture of gunpowder. A special assignment in 1798 was to visit and evaluate the Natron Lakes, a series of small lakes located in a depression, below sea level, in the desert about 45 miles northwest of Cairo. The Natron Lakes were of interest because they were bordered by a thick crust of natron (hydrated sodium carbonate). Berthollet's observations at the lakes led to a problem in interpretation. Berthollet knew that the reaction

\[
\text{Na}_2\text{CO}_3 + \text{CaCl}_2 \rightarrow 2\text{NaCl} + \text{CaCO}_3
\]

goes essentially to completion in the laboratory. In the Natron Lakes, where salt water and underlying limestone were in contact, this reaction seemed to be partially reversed. Such a reversal is contrary to the doctrine of elective affinity, which postulates all-or-none reactions. The unexpected phenomenon at the Natron Lakes led to an "Aha!" insight for Berthollet. He correctly inferred that chemical reactivity depends not only on the "elective affinities" of the reactants, but also on the relative masses of reactants and products. His conclusions, publicized in a lecture in Egypt (10) and in greater detail in an 1801 volume (11), constituted the first qualitative presentations of the concepts of reaction reversibility, equilibrium in chemical reactions, and the role of the masses of reactants and products in establishing the position of equilibrium in a given reaction. By the time of the 1801 volume, Berthollet was able to give other instances where a reversal of an expected reaction could be observed. These typically involved solubilizing a relatively insoluble product: barium sulfate, calcium oxalate, or calcium phosphate, for example.

Consider as an illustration the reaction:

\[
\text{Ba(OH)}_2 + \text{K}_2\text{SO}_4 \rightarrow 2\text{KOH} + \text{BaSO}_4
\]

Berthollet showed that treatment of barium sulfate with potassium hydroxide in boiling water gave a solution containing potassium sulfate. Furthermore, with a large excess of potassium hydroxide, the barium sulfate could be almost completely dissolved. In his 1801 book Berthollet summarized his conclusions (11):

The doctrine of Bergman is founded entirely on the supposition that elective affinity is an invariable force, and of such a nature, that a body which expels another from its combination, cannot possibly be separated from the same by the body which is eliminated. It is my purpose to prove that elective affinity, in general, does not act as a determinative force, by which one body separates completely another from a combination; but that, in all the compositions and decompositions produced by elective affinity, there takes place a partition of the base, or subject of the combination, between the two bodies whose actions are opposed; and that the proportion of the partition are determined, not merely by the difference of energy in the affinities, but also by the difference of the quantities of the bodies; so that an excess of quantity of the body whose affinity is the weaker, compensates for the weakness of affinity.

If I can prove that a weaker degree of affinity can be compensated by an increase of quantity, it will follow, that the action of any body is proportionate to the quantity of it which is necessary to produce a certain degree of saturation. This quantity, which is the measure of the capacity of saturation of different bodies, I shall call mass [Emphasis by Berthollet].

Berthollet's concepts were qualitative in nature, and there was no quantitative development for many decades. Why was this so?

**Quantitative Developments:** **Reaction Kinetics and Equilibrium**

Berthollet's mass action ideas were well ahead of his time. Only in 1850 did the German chemist Ludwig Wilhelm publish the first quantitative measurements of the rate of a chemical reaction, the acid-catalyzed inversion of sucrose. Wilhelmy showed that his data could be fitted by a rate equation corresponding to a pseudo first-order irreversible reaction.

Extensions of Wilhelmy's work to the kinetics of a reversible reaction did not occur for more than another decade—by Marcelin Berthelot and Péné de St. Gilles in France (1862-1863) and by Cato Maximilian Guldberg.
and Peter Waage in Norway (1864, 1867, 1879). Meanwhile, Augustus G.V. Harcourt and William Esson at Oxford (1865-1867) published rate laws for complex irreversible reaction schemes, e.g., a series reaction in which the first step is first-order and the following one is second-order.

We return to the question of why there was a fifty-year delay in creating a quantitative framework for Berthollet’s ideas and can only speculate about its answer. Of several possible contributing factors, one may be the slow realization that quantitative physical laws had important applications in chemistry. Physical chemistry was explicitly recognized as a new subdiscipline only in the latter half of the nineteenth century. Another contributing factor was the common failure of authors to reference earlier work by others; and the multiplicity of European languages was a further deterrent. Berthollet and Berthelot published only in French; Wilhelmy only in German; Harcourt and Esson in English; and the first paper of Guldberg and Waage appeared in Norwegian. Wilhelmy’s 1850 papers included no mention of Berthollet’s publications fifty years earlier. In turn, Wilhelmy’s studies of sugar inversion went unnoticed and were not mentioned by either Berthelot and St. Gilles, Guldberg and Waage, or Harcourt and Esson. The first citation of Wilhelmy was by Ostwald in 1884 in the context of his own research on the same reaction, the inversion of sucrose (12). Of historical interest is the seminal 1889 paper of Svante Arrhenius (13), in which the exponential dependence of rate constant on temperature in the inversion of cane sugar by acids was proposed.

The papers of Harcourt and Esson, published several years after the 1862 publications of Berthelot and St. Gilles, show no awareness of Berthelot’s work on kinetics or of Guldberg and Waage’s 1864 publications. Finally, although Guldberg and Waage in 1864 referenced the 1862 experimental results of Berthelot and St. Gilles, they ignored Berthelot’s own theoretical treatment of the kinetics for a reversible reaction—even as a subject for criticism.

On the other hand, Berthelot’s work on equilibrium was explicitly cited with admiration by his eminent countryman, Berthelot, some sixty years later. The astonishing story of Berthelot, a founder of thermochemistry, pioneer of organic chemistry, discoverer of the explosion wave, and foreign minister of France, among other things, warrants a separate communication.

REFERENCES AND NOTES

9. A literary sidelight: An 1809 novel of Goethe was entitled Die Wahlverwandtschaften (Elective Affinities), the title being taken from Bergman’s treatise on chemical reactivity. Goethe’s story described doomed lovers who are unwittingly drawn to one another, leading to the breakup of the marriage of one and to the death of the other. The novel treats sexual attraction in chemical terms. Not surprisingly, it was banned as immoral.

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DOBEREINER'S HYDROGEN LIGHTER

William D. Williams, Harding University

Before the invention of matches, the "Dobereiner Hydrogen Lamp" was an ingenious device that furnished an instantaneous flame. Used somewhat like a present-day cigarette lighter, it gave, at the push of a finger, a flame that could light a candle or a wood splint. From its introduction in 1824 until the widespread use of friction matches (1) in the 1840s, the hydrogen lighter was a household and laboratory appliance. Johann Wolfgang Dobereiner (2) had made the curious observation that a jet of hydrogen gas flowing into spongy platinum caused the platinum to become so hot that it ignited the hydrogen stream. The application in a rapid lighting device was possible because the apparatus design allowed a self-regulating on-off control of the chemical reaction releasing the hydrogen.

The inner glass tube (b) was open at the bottom and cemented air-tight into the brass cover, so as to connect with the external stopcock (3). The outer glass vessel was filled with dilute sulfuric acid. A piece of zinc (c), suspended in the acid on a brass or platinum wire, allowed the generation of hydrogen gas, which rose to the top of the inner vessel. With the stopcock closed, the gas pressure would push the liquid below the zinc and the reaction would cease. To obtain a light, the stopcock would be opened, and the hydrogen stream would contact the spongy platinum (a) and quickly ignite, the flame being emitted through (a). As long as the stopcock was open and the gas pressure released, the acid would rise to contact the zinc and continue to produce more hydrogen. Closing the stopcock would extinguish the flame, and gas pressure would again push the acid off the zinc, the reaction being stopped.

When Dobereiner demonstrated the ability of spongy platinum to ignite a jet of hydrogen before a scientific gathering in Halle on September 18, 1823, Berzelius declared it the most astounding discovery of the time. About 20,000 Dobereiner lighters were in use in Germany and England by 1828. Dobereiner realized little profit, however, because he held no patent for the invention (4). It should be noted that a hydrogen generating vessel similar to the above design, but without the platinum ignition part, was in use before 1823 (5). Dobereiner merely adapted that apparatus to his platinum ignition discovery.

The hydrogen lighter must have been common in the United States, too, because it appeared, in a variety
of construction designs, in many 19th-century textbooks (6). One design even featured a spring lever stopcock handle, making it thumb-controlled when held in one hand (7). A quaint 1839 American children’s chemistry book presented the hydrogen lighter as a common household utensil, even used by young children (8):

And how shall we make some hydrogen?
Why you have made it many a time.
When?
Have you not often lighted a candle from the glass jar on my table?
Yes; but did I make hydrogen then?
That jar contains some water and sulphuric acid mixed, and that piece of metal that you see hanging by the wire is zinc.

Figure 2. Thumb Action Lamp (see Ref. 7)

Following that quotation there was a diagram of the jar with further discussion of how it worked. The sulphur(sic) chapter of the same book included an added comment: “our hydrogen jar is quite as convenient as matches. Yes: it has not the unpleasant odor of matches, while it is as cheap, if a light is often wanted (8).” [See also Ref. 1.]

The size of the Dobereiner jar is unclear, but a contemporary American science apparatus catalog advertised three sizes, priced at $2, $3, and $4 (9). While no mention of safety is found in any reference to the apparatus, one wonders whether there were accidents from hydrogen explosions or acid spills.

The hydrogen on-off control of the Dobereiner lamp will be recognized as a forerunner of the Kipp gas generator, common in laboratories until metal gas cylinders became the typical source of supply. Indeed, an 1831 design of the Dobereiner lighter was remarkably similar to the Kipp apparatus (10). The Kipp generator, sometimes as tall as two feet, is still found in some current laboratory supply catalogs.

Even after the availability of matches, the Dobereiner lamp continued to be used for laboratory demonstrations until late in the 19th century. Some should have survived, but the author is unaware of any. Readers who know the location of any specimens should notify the author or editor.

REFERENCES AND NOTES

1. Sulfur tipped splints were in use from the turn of the 19th century, but an existing flame (from flint, steel, and tinder box), was required to ignite them. Various other methods for chemical fire were troublesome—requiring sealed containers for dangerous phosphorus or concentrated sulfuric acid bottles into which chemically tipped matches were dipped. The first practical friction matches, called “lucifers,” were produced in England in 1827. Various compositions for the striking head were developed during the 1830s and 1840s. Matches were not common in the United States until the 1840s and even later on the frontier. For a history of matches, see M. Crass, “A History of the Match Industry,” J. Chem. Educ., 1941, 18, 116, 277, 316, 380, 428.

2. acy at the University of Jena, Germany, is best known for his “triads,” which contributed to the systematic classification of the elements and the development of the periodic table. For biographies, see Ref. 4.

3. J. Hyatt, The Elements of Chemistry, Clark, Austin & Smith, New York, 1856, 47.


6. rdson and Lord, Boston, 1827, 151; J. Webster, A Manual of Chemistry, Richardson and Lord, Boston, 1828, 118;


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**HOPOS 2000**

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BOOK REVIEWS


From the 1960s to the early 1990s anyone wanting a recent history of chemistry had essentially two choices: Aaron J. Ihde's one-volume treatment or the multi-volume work by J.R. Partington. Both were intended to be comprehensive surveys, both organized along the lines of a chronological narrative, and both written by chemists. Since 1990, however, there has been an embarrassment of riches with the appearance of a dozen general and specialized histories of chemistry.

In this burgeoning list A History of Chemistry offers something fundamentally different; it is an alternative, as well as a direct challenge, to traditional histories of chemistry. Written by a professional historian of science (Bensaude-Vincent) and a professional philosopher of science (Stengers), this text provides a counterpoint to the notion of a seamless narrative of chemistry. Consisting of five individual "snapshots" of chemistry, it offers many fascinating vignettes, written in a lucid, readable style—a tribute to both the skills of the translator and the original French text produced by the authors.

Bensaude-Vincent and Stengers approach their subject on the basis of assumptions that many chemists may not hold. Unlike those chemists whose histories often served as "manifestoes for their science [and] described a chemistry that was sure of its identity—and of its successes as well," these authors are not at all sure of that identity. In fact, they adopt the "quest for the identity of chemistry" as their guiding principle for this narrative. The central question "What is chemistry?" leads them to pose additional questions:

What if, instead of digging out the hidden past of a well-defined science whose identity is not in question, we envisage this science as the product of a history? What if, instead of saying that chemistry has a history, which one can choose to study or ignore, we propose that it is a history in progress?

According to the authors, a history based on the answers to these questions "would less resemble the triumphal march of a science that is sure of itself than a long chain of events shaping a science that is haunted by questions of its nature." But despite their claims that the "place of chemistry in the hierarchy of the sciences was always a matter of debate" and that chemistry has been continually obliged to renegotiate its relationship with the other sciences, Bensaude-Vincent and Stengers do not show chemistry to be unique in this regard. Nevertheless, working from the assumption that "there is no eternal essence of chemistry, no transcendent object that is unveiled over the course of the centuries," the authors free themselves to look for "chemistry's successive identities" over a long global history. These they organize into the five chapters, each of which "presents a different face of chemistry [and] delineates its identity at a given time."

The first of these five snapshots provides a glimpse at some of chemistry's origins in alchemy and in the 17th-century revival of certain Ancient Greek ideas about matter. The second and third chapters are surveys of 18th- and 19th-century chemistry, respectively. In Chapter 4 the authors meander through several areas of in-
industry associated with chemistry, and in the final chapter they offer samples of chemistry from the 20th century. There is also a short epilogue. In all these chapters the authors "paint broad historical pictures" from which, they argue, "it is possible to understand all the industrial and intellectual adventures that at various periods have shaped chemistry's successive identities . . ." We believe that the shortcomings of this approach outweigh its advantages.

In the opening chapter, "Origins," Bensaude-Vincent and Stengers find ideas in Greek thought from Thales to Aristotle that obsessed and still obsess chemistry—principles, elements, atoms, the problem of differentiation, the relationship between the one and the many, generation interpreted as an ephemeral transgression of a static order or as a result of perpetual conflict. A list of ideas that have infused chemical thinking for more than 2000 years suggests their longevity even if they do not represent a continuous tradition. It is true that Dalton's atoms were not identical to those of Democritus and Leucippus, but the choice of the term "atom" in the early 1800s was not arbitrary.

This opening chapter also covers the link from alchemy to chemistry. Just as the authors "find the description of procedures . . . that create a practical continuity between alchemy and chemistry," they also find a theoretical continuity, largely on the basis of Paracelsus, who is termed "the best known of the sixteenth-century chemists." The authors cite other transitional figures—van Helmont, Glauber, and Becher—as participants in an "indecisive struggle between rival doctrines," the outcome of which was not at all clear at the time. But the authors do not make it clear either how that struggle proceeded or what events and issues determined its outcome.

Broad strokes are also problematic in the third chapter, "A Science of Professors." Bensaude-Vincent and Stengers describe Paris as "the center of European chemistry" in 1800, but they give little indication that the center ever moved during the 19th century. This chapter presents an interesting overview primarily of French chemistry, though Kekulé, Mendeleev, and Faraday do flit across a few of its pages. The cameo role of Faraday is typical. His contributions to electrochemistry are listed as a chemical interpretation of the battery, the introduction of the terms "anode" and "cathode," and the laws of electrolysis. The authors sketch out Faraday's electrochemistry in little over half a page, less than the space they devote later in the chapter to Dumas' rejection in 1836 of Avogadro's hypothesis and of atomic theory in general.

Chapter 5, "Dismembering a Territory," returns to this antiatomism as still significant as late as the beginning of the 20th century.

In 1910 many specialists in inorganic chemistry still thought that the atomic and molecular hypothesis was only a fiction and criticized the way those unobservable entities were presented as if they really existed.

. . . But if the atom provoked skepticism from inorganic chemists, it was the target of much more radical questioning from two renowned physical chemists, Pierre Duhem and Wilhelm Ostwald.

As committed positivists, these "two renowned physical chemists" hardly represent mainstream views in turn-of-the-century chemistry. Duhem, a professor of theoretical physics, rejected the scientific validity of any kind of model of matter; and Ostwald, one of the last chemists to oppose atomic theory, had retreated so far into energetics that he seemed to deny the existence of matter as commonly understood by other scientists at that time. It is certainly true that many chemists throughout the 19th century were skeptical of the Daltonian atom, and French scientists were among the most vigorous antiatomists. But even those who doubted the physical existence of atoms usually found the concept useful in explaining chemical phenomena, and many chemists did not regard atoms only as "fictions whose pretension to reality was by definition temporary and relative to their ability to organize the facts." In this, as in other instances, Bensaude-Vincent and Stengers do not do justice to a very complicated story.

The authors make many other claims that call for greater discussion than they provide—chemistry is the "daughter of speculative alchemy" (p 209); chemistry is now little more than "a service science, subordinated to physics, and in the service of biology and industry," apparently with no identity of its own (p 253); and "today 'purity' appears to be the prerogative of physics" rather than chemistry (p 256).

In addition to statements that are open to debate, this book contains statements that are mistaken in fact—Volta's "pile . . . generated electricity, as a Leyden jar does" (p 108); and "Wollaston . . . preferred to determine all these equivalent weights in relationship to the basic unit O = 100" (p 117). There are also statements whose meaning is not readily apparent to us—"it is always useless to rewrite history" (p 231); chemical equi-
librium is "the state in which the rates and affinities are simultaneously zero [and] is no longer a privileged state, but only the state to which irreversible processes lead" (p 249); and "if the activity in chemistry becomes more abstract, it also tends to escape subordination to physical law" (p 261).

The potpourri of topics in Chapter 5 does not provide a representative picture of 20th-century chemistry. Instead, the authors select topics that tend to be allied with physics and thus support their view that "chemistry may seem to be a kind of applied physics" (p 245). For example, they include some discussion of the work of Ilya Prigogine in connection with nonequilibrium systems and dissipative structures, which are an important, but minor aspect of contemporary chemistry. Neither the general list of references nor footnotes cite any publications of Prigogine, nor even *Order Out of Chaos* (1984), which he co-authored with Isabelle Stengers. There are other omissions and numerous errors in the references as well.

All told, these are not qualities that recommend *A History of Chemistry* as a text for undergraduate courses in the history of science or for "a wider nonprofessional public," as one blurb on the dust jacket suggests. This text raises philosophically complex issues about the nature of historiography: the aims, methodologies, and the agendas and biases of chemists, as well as those of historians, who write histories of chemistry. These are not issues for the neophyte or the generalist.

Bensaude-Vincent and Stengers clearly intend their history of chemistry to be provocative, and it is, but it is most appropriate for readers who are already familiar with the subject. These individuals can certainly profit from this particular history whether they are sympathetic to a postmodernist reading of history or not. This book raises fundamental and disquieting questions, which challenge chemists with a historical bent to re-examine their views and attitudes about the history of their own science. Chemistry shouldn't ever be the same.
contributions are those by Ernst Homburg on the many contexts of the emergence of the German chemical profession in the first half of the nineteenth century, Nathan Brooks on the emergence of academic chemical profession in Russia, and Kostas Govraglu on the cultural and intellectual issues facing natural philosophers and chemists in nineteenth century Greece. Colin Russell’s chapter on chemistry in Sweden seems curiously out of place in the context of the volume, as it merely recounts the discoveries made by Swedish chemists and neglects the issues of professionalization altogether. The two most glaring omissions among European countries are the Netherlands and Switzerland, and it is not obvious why they were not included.

Despite the wide range of countries covered, there are remarkable similarities in the professionalization of chemists during the nineteenth century. There was everywhere a tension between practical and academic chemistry, and chemistry as a science emerged only slowly from medicine and pharmacy. Training of chemists took place at both the universities and the technical institutes, and there was always a tension between them as to what that training entailed. A common theme is the tendency of nearly all countries by mid-century to emulate the model of the teaching laboratory at the German universities begun by Friedrich Stromeyer at Göttingen and made spectacularly successful by Justus von Liebig in Gießen. Also clear is that, although Germany lagged behind France (where, Crosland reminds us, in the early century chernistry was second only to mathematics in prestige) and Britain in the training and practice of chemistry, within the space of 50-60 years, it surpassed both of these countries to become the undisputed leader in the practice of chemistry and in chemical education.

The issues involved in understanding the process of professionalization are extraordinarily complex, involving broad cultural, intellectual, and political issues that are unique to each country. This volume offers an excellent overview of the issues historians must face when confronting the problem of characterizing the nature of professionalization in chemistry specifically and the sciences in general during the nineteenth century.

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Over twenty years ago, B. J. T. Dobbs argued in The Foundations of Newton’s Alchemy that Isaac Newton was deeply involved in alchemical practice. In doing so, Dobbs brought to light a major aspect of Newton’s life (he wrote over a million words on alchemy, far more than he wrote in physics) that previous biographers had considered “embarrassing” and attempted to explain away. In Aspiring Adept, Principe draws on extensive, previously unexamined archival sources to reveal that Robert Boyle, long considered to be the “Father of Modern Chemistry,” was as thoroughly involved in alchemy as his younger colleague Newton. The resulting book is of remarkable significance for our understanding of Boyle’s place in seventeenth-century science and within the history of chemistry.

Alchemy as an historical human activity has all too often been relegated to pseudoscience and treated as an irrational enterprise undertaken by “unenlightened” people in a “pre-scientific” age. For this reason Newton and Boyle have long been considered to have been “above” the practice of alchemy. According to Principe, this unfortunate consequence has its roots in two historiographic mistakes: 1) the tendency to regard Boyle and Newton as “modern scientists” and therefore read their work as “precursors” to our own ideas about nature, and 2) a general lack of understanding of (admittedly extremely difficult) alchemical theory and practice, specifically the tendency to lump “alchemy” into a single monolithic philosophy of nature. One of Principe’s most valuable contributions in this book is to initiate a recasting of “alchemy” into several different activities, and to illustrate the subtlety of the relationships between alchemy and religion. In order to avoid confusion over the meaning of the terms “alchemy” and “chemistry,” which shifted enormously in their meanings both during and after the seventeenth century, he reintroduces the archaic term “chymistry,” to mean the sum total of chemistry/alchemy in the seventeenth century, and re-
vives the Greek term "chrysopoeia" for that specific area of chymistry concerned with transmutation, and "spagyria" to refer to the drawing out of essential principles for later recombination and purification.

Principe begins with a thorough examination of historical portrayals of Boyle, beginning with the collection of his papers in the seventeenth century. Very soon after Boyle's death in 1691, Boyle's alchemical works were ignored and forgotten in the creation of his collected works, in the attempt to cast him as a "rational" thinker like Newton, in opposition to alchemy, which even by the early eighteenth century had come to be viewed as "irrational" and suspect. Ever since, Boyle has been stripped of much of his seventeenth-century identity and cast impossibly as a "man ahead of his time" who eschewed "mystical" alchemy for the mechanical philosophy. By the mid-twentieth century, this view of Boyle as a "modern" scientist continued in the work of Marie Boas Hall, arguably the most influential Boyle scholar of the mid-twentieth century, who treated Boyle as a prelude to Lavoisier. In an insightful metaphor given by Principe, the resulting conception of Boyle was not of "a seventeenth century natural philosopher, but ... [of] a chemical John the Baptist."

Beginning his study of Boyle proper, Principe turns first to an analysis of the Sceptical Chemist, one of the most famous and difficult books in the history of chemistry. The fame of the Sceptical Chemist has previously rested solely on the very short passage, quoted in endless histories of chemistry, in which Boyle denounces the definition of chemical elements. While it has long been known that this passage did not in fact deny the existence of elements, the book as a whole has escaped the scrutiny of historians. Principe provides the first thorough historical analysis of the argument of, and audience for, the Sceptical Chemist and argues that Boyle directed it not toward "alchemists" per se, but toward a specific group of chymists: the Paracelsian chymists and systematizers who attempted to create entire chymical systems on the basis of only a few observations. It was decisively not a rejection of alchemy. Concurrent with Principe's analysis is the recognition that chymists as a group belonged to many different schools; it is impossible to categorize them together.

The next three chapters are devoted to showing that Boyle, in addition to not rejecting alchemy, actively embraced it, writing treatises with alchemical motifs, corresponding actively with practicing alchemists, and practicing alchemy itself. Chapter three introduces the Dialogue on Transmutation, a fragmentary unpublished document, set as a Galilean-type dialogue between two groups of chymists discussing the existence of the philosophers stone. As the Dialogue proceeds, Boyle leaves no doubt that the group of chymists defending the philosopher's stone is correct. The Dialogue is a major work, offering crucial insight into the kind of alchemical pursuits that interested Boyle. Chapter four looks at the role of "transmutational histories," or accounts of transmutations by various alchemical adepti (some traveling from town to town) that became famous throughout Europe. It seems clear that Boyle directly witnessed such transmutations several times and actively pursued, and would pay for, alchemical knowledge from the adepti that came to his attention. In chapter five, Principe demonstrates that Boyle himself attempted to uncover the secrets of the adepti, both in his intensive study of the metaphorical and secretive texts of chrysopoeic alchemy, and by his own laboratory experiments. Significantly, Boyle's own chrysopoeic and spagyric manuscripts were written in a system of often simple codes that he did not use in other contexts. In order to show Boyle's intense interest in experimental chrysopoeia, Principe traces Boyle's forty-year quest, documented in both archival and printed sources, for the philosophical mercury needed for preparing the philosopher's stone.

In the last chapter, Principe suggests three motivations for Boyle's intense interest in alchemy. The first is what we would call scientific—chymistry's value for furthering the practice of natural philosophy. As the philosopher's stone also offered the promise of a "universal medicine," Boyle found medical reasons for pursuing alchemy. The most startling motivation Principe uncovers, however, is the role of the philosopher's stone as an intermediary between the corporeal and spiritual worlds. If made, Boyle believed that the stone would attract angels. While at first this would sound fantastic and unbelievable, this belief in fact ties together Boyle's twin interests in the mutually antagonistic realms of corpuscular philosophy and Christian theology. As a devoted Christian, Boyle felt compelled to refute the atheistic implications of the mechanical philosophy and to understand how the incorporeal world of the angels could interact and intervene with the physical world.

Having thoroughly reconstructed Boyle as a devoted alchemist intensely interested in the chrysopoeic arts, Principe motivates us to rethink his place in seventeenth-century science. If he is not the "Father of Modern Chemistry," why is Boyle important? Rightly, Principe does not discard the importance of Boyle by denying entirely his influence on later generations, but
attributes the apparent conflict between Boyle as a modern and Boyle the alchemist as a previous deficiency of historians to see that a chymist in the seventeenth century possessed aspects of both. Further, because Boyle's corpuscularianism was likely itself derived from the alchemical tradition, we must consider the development of chymistry in the seventeenth century more evolutionary than revolutionary.

There are three appendices containing previously unpublished alchemical works of Boyle. The first and largest appendix is the extant Latin text of the Dialogue on Transmutation, reconstructed by Principe from twenty-three existing archival fragments, with an English translation on facing pages. Appendix Two contains other accounts of transmutations obtained by Boyle through interviews and prefaces to Boyle’s other chrysopoeic works whose full texts have not survived. The third appendix contains a dialogue on the conversation with angels aided by the philosopher’s stone.

In the end, we should not be too surprised that Boyle was interested in alchemy. After all, Boyle was a man of the seventeenth century, a period in which alchemical practice flourished before it disappeared in the eighteenth century. Because nearly all major natural philosophers in the seventeenth century England—Newton, Locke, Dee, Ashmole, Starkey, among others—were intensely involved in alchemy, we should be more surprised to find that Boyle was not involved in alchemical pursuits. Aspiring Adept is a rich work that should change the way we present Boyle in a history of chemistry course. For those interested in the history of alchemy, the relationships between “chemistry” and “alchemy,” the emergence of the former from the latter, or the place of Boyle in the Scientific Revolution, it is required reading. Peter J. Ramberg, Max-Planck Institute for the History of Science, Wilhelmstraße 44, D-10117 Berlin, Germany.


Readers are invariably surprised, on encountering a book about the history of women in science, by the number of women who have made significant contributions to mathematics, chemistry, physics, and the biological sciences. After reading about these women’s accomplishments, however, the reader is often disappointed by the paucity of information available on both their personal and professional lives. A new book that attempts to fill this void was recently published by the American Chemical Society and the Chemical Heritage Foundation. Written by a wife and husband team, the Rayner-Canhams’ latest book, Women in Chemistry: Their Changing Roles from Alchemical Times to the Mid-Twentieth Century, containing 207 pages of text and 45 pages of references and notes, introduces the reader to more than 100 female chemists and physicists by name, as well as a few whose names have been lost. Although the authors do an excellent job of presenting a broad spectrum of women chemists, they, too, admit at the end of the book, “It is unfortunate that we have so little record of the feelings of these individuals.” In spite of this admission, the authors have made a significant contribution to the histories of women in chemistry. They have introduced us to many important women chemists and piqued our interest in learning even more about their personal and professional lives, as well as about how they interacted with their contemporaries as scientists.

The Rayner-Canhams are on the faculty of Sir Wilfred Grenfell College, Newfoundland, Canada, where Marelene is a Laboratory Instructor in Physics and Geoffrey is a Professor of Chemistry. They previously collaborated on A Devotion to Their Science: Pioneer Women of Radioactivity, a compilation of the lives and work of 23 women researchers who made contributions to the new fields of radiochemistry and nuclear physics in the early part of the twentieth century. Their
extensive research into the history of women in science uniquely equips them to tackle a book of this scope.

They begin the book with women who developed methods for extraction and distillation of plant compounds in Mesopotamia around 1200 BC and end with women of the 20th century who did their significant work before 1950. Although many of these women are linked to important scientific discoveries, in most cases only bits and pieces of their individual experiences have been preserved to help us understand and appreciate both their struggles and their contributions.

The authors' stated perspective in presenting their material was to "provide the context required by science historians," rather than simply to recount the biographies of individual female chemists. This is certainly a useful approach, especially considering the major influence that society, as well as cultural and historical events, exerts on the practice of science. The historical context is divided, as the book progresses, into three major subdisciplines of chemistry in which women were particularly active in the 20th century: crystallography, radioactivity, and biochemistry. A chapter on women's contributions to industrial chemistry, analytical chemistry, and chemical education, and as historians of chemistry is followed by a final chapter that draws some general observations and conclusions about women chemists in the 20th century.

Based on this historical-context approach, the first chapter offers a brief overview of women chemists prior to the Scientific Revolution (pre-eighteenth century). These women are collectively referred to as alchemists, although they made discoveries of lasting scientific importance to which their names are still attached. Among them is Maria Hebraea, who lived and worked in Alexandria during the early centuries AD. Her name is immortalized by her invention of the heating and distilling apparatus called the bain Marie, or water bath—the French bain Marie and the German Marienbad—which had a glass component so that reactions could be observed without interruption. The names of a number of Chinese female alchemists have also survived, as have those of highly educated abbesses who left written accounts of their scientific contributions made during the Dark Ages. The writings of several European women who had a passion for chemistry (or alchemy) during the 16th and 17th centuries provide a tantalizing glimpse into the frustration that these women felt as formal university programs were established for men only in France and England. The notable exception was in Italy, where women had some access to universities at the beginning of the 18th century. Queen Elizabeth I reinstated the complete ban on women at universities and issued the order that academic celibacy be continued in Britain, an order that was observed at Oxford and Cambridge Universities until 1882.

Women chemists in the 18th and 19th centuries are divided into two groups, chemist-assistants of the French salons and independent researchers. A biographical sketch of Marie Anne Paulze-Lavoisier (1735-1820) is one of the most satisfying in the entire book. It covers the many-faceted life of this remarkable woman, who actively participated in the controversial scientific and political events of her time, assisting her famous husband Lavoisier until he was decapitated during the French Revolution. Several of her contemporaries are also mentioned, but there is no discussion of their influence on each other, although they were almost certainly acquainted. Is the record silent on this point? The reader would like to know. Among the independent researchers who made noteworthy contributions was Elizabeth Fulhame (late 1700s), who is credited with the first recorded experiments on photochemical imaging, the first proposal of a two-step chemical reaction, and the first published concept of a catalytic process. She was elected a corresponding member of the Chemical Society of Philadelphia, and her discoveries were acknowledged by leading chemists in both the U.S. and Europe. At about the same time, Jane Marcet (1769-1858) wrote her popular book for young ladies, entitled Conversations on Chemistry, which went through 23 impressions in the U.S. Other important members of this group of "amateur chemists" were Helen Abbott Michael and Agnes Pockels, whose name is still associated with important results of her well-documented experiments, carried out in her kitchen, which contributed to the origins of surface science.

As the 20th century began, access to higher education became the key for women's participation in chemistry. Pioneers who opened the doors for women included Ellen Swallow Richards (1842-1911) at Massachusetts Institute of Technology and Rachel Lloyd (1839-1900), who received her Ph.D. in Zurich, Switzerland, and returned to the U.S. to make her mark as a professor and researcher at the University of Nebraska. Laura Linton (1853-1915) followed a well-traveled path from chemistry teaching and research into a career in medicine at age 47. Although there is no further mention of women who made the transition from chemistry into medicine, more examples are no doubt available and would have made interesting reading.
The discussion of women in crystallography gives well deserved credit to W.H. Bragg, W. L. Bragg, and J. D. Bernal for the mentoring support that they provided women scientists. Biographical sketches of Kathleen Lonsdale (1903-1971), Nobel Prize winner Dorothy Hodgkin (1910-1994), and Rosalind Franklin (1920-1958) provide an overview of both exciting developments in crystallography and the important historical changes taking place at British universities during the first half of the 20th century. Two particularly appealing photographs of Hodgkin and Franklin as young women are excellent additions to the text. A number of other female crystallographers are briefly mentioned. Completing this chapter should motivate the reader to undertake a search for more information about these fascinating and important female crystallographers; additional information is easy to find and well worth the effort.

The account of women in radioactivity is dominated by Marie Sklodowska Curie (1867-1934) and her daughter Irene Joliot-Curie (1897-1956), who both won the Nobel Prize in Chemistry for their contributions to this burgeoning field of research. Their life stories are already familiar to many readers, but some of their colleagues have long gone unnoticed. More insight into the lives of Norwegian chemist Ellen Gleditsch (1879-1968) and Viennese chemist Stefanie Horovitz (1887-1940), who was a victim of the Nazi purges, would help balance the record. Several women who were physicists, rather than chemists, are also included in this chapter, probably because of the interdisciplinary nature of nuclear science.

Some of the most interesting material in the book concerns women in biochemistry whose lives and careers have been similar to those of women currently working in the chemical professions. The founder of modern biochemistry and the primary mentor for women in this field was F. Gowland Hopkins of Cambridge University. His counterpart in the U.S. was Lafayette Mendel at Yale University; he trained 124 PhDs, 48 of whom were women. Icie Macy Hoobler (1892-1919), who was one of Mendel's most famous female students, and her list of important accomplishments includes being the first woman to chair a local section (Detroit) and the first woman to chair a division (Division of Biological Chemistry) of the American Chemical Society. Two other women in this category are Nobel laureates: Gertrude Elion (1918-1999), who rose to prominence at Burroughs Wellcome, and Gerty Radnitz Cori (1896-1957), who finally was made a full professor at Washington University in St. Louis after she and her husband were awarded the Nobel Prize in 1947.

Inclusion of more information about the Garvan medalists of the American Chemical Society, from the list of 34 winners between 1937 and 1976 as listed in the appendix, would have been of great interest to many readers. In particular it would have been appropriate to include Dr. Marjorie Vold, who served on the faculty of the University of Southern California and represents the small, but important, number of women chemists who were professors at major universities. There is one brief reference to women's contributions to cosmetics chemistry in the biography of Florence E. Wall (1893-1988). Formulation of cosmetics is a recognized extension of chemistry and one in which women have made major contributions, including those of the famous and successful African-American entrepreneur, Madame C. J. Walker (1867-1919). Although not a trained chemist, she deserves recognition for her original formulations of products in this industry.

A history of women in chemistry would not be complete without acknowledging the contribution to the chemical education of women made by Emma Perry Carr (1880-1972), who was personally responsible for establishing at Mount Holyoke College an undergraduate chemistry department which was the equal of any in the country. One of the most memorable quotes in this entire book is that of a mourner at Carr's memorial service who remarked, "It was a resistant person who could fail to share her enthusiasm whether for science, for politics, for her family, for pi electrons, for baseball, or for the circus." Many of the women who are pursuing chemistry today can look back with appreciation to Emma Carr, who instilled that enthusiasm for chemistry and life in general into her young students. As this book closes with a review of the decades from 1900 to 1950, the picture is far from rosy. After two world wars had opened doors to entry-level positions for women in government, industry, and academe, many found the doors closed just as surely as an apparent new world order loomed into view. The promise of equal participation for women in chemistry was still a chimera, and the second half of the 20th century has continued to present many of the same challenges for women chemists. One of the values of reading this book lies in the reader's realizing that women can and have made outstanding contributions to chemistry in spite of the barriers that still exist to their full participation in a discipline in which gender distinctions certainly should have no place.
This is a book that should be read and retained for ready reference by anyone interested in the history of women in chemistry. It contains a wealth of well-organized information and provides excellent suggestions for further exploration of the subject. It would be especially appropriate for use in a course on the history of chemistry. Mary F. Singleton, 597 Gerard Court, Pleasanton, CA 94566.

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This thoroughly researched, detailed biography of the Nobel Prize winner Fritz Haber, coming 65 years after his death, is a rich source of information, not only about Haber's life and scientific activities but also about the climate of chemistry in Germany before and after World War I. It is a welcome resource and quite in contrast to the only brief biography in English [M. Goran, *The Story of Fritz Haber*, University of Oklahoma Press, Norman, 1967, 176 pp, octavo], in which, according to Stoltzenberg, much of the anecdotal material, derived from friends and relatives of Haber, is of questionable validity. A novel about Haber by H. H. Wille, *Der Janus-Kopf*, Buch Club 65, Berlin, was published in 1970.

The author, Dietrich Stoltzenberg, born in 1926, was trained as chemist at Karlsruhe under Criegee and spent his career in German chemical industry. He is the son of Hugo Stoltzenberg, chemist and manufacturer, who was in close communication with Haber in the early 1920s, after WW I, in connection with disposal of chemical warfare materials and the building of manufacturing plants in Spain and the Soviet Union, as well as in Germany. The relationship with Haber ended abruptly in 1925, when, in a confrontation between IG Farben and Hugo, Haber withdrew his support of Hugo in favor of the industrial giant. In spite of this, the author seems to present a highly objective picture of Haber, even in instances where he was at odds with Hugo Stoltzenberg.

The author has taken advantage of rich sources for this biography. A major resource is the archival material at the Max-Planck-Gesellschaft, Berlin-Dahlem, consisting of the papers (Nachlaß) of J. Jaenicke, together with many other materials he collected over a 20-year period, in anticipation of the preparation of an authoritative biography, which he never realized. Many other archival sources are cited, including private papers of Hugo Stoltzenberg and his wife, now in the possession of the author Dietrich; others in Germany, including some from the former DDR; documents from Israel, Cal/Berkeley (Emil Fischer Nachlaß), and Cal Tech.; and the autobiography of Charlotte Nathan Haber, Haber’s second wife. The author notes that records of the WWI chemical warfare program were either destroyed or may be in archives of the former Soviet Union. Stoltzenberg spent eight years researching the myriad documents for the biography.

The language of the text is eminently readable for a non-German who has the fundamental grasp of the language. Sentence structure is straightforward, and the text is practically error-free. This reviewer noted only
two typographical errors (pp 32, 286) and one (p 124) for the date (1891, not 1899) of Haber's completion of the doctorate. The book is generously illustrated with 93 photographs, mainly of family members and collaborators, some from the author's own collection. The index for such a long book seems thin, with only a little over 300 entries. "Chlor" but not "Brom" is included, even though both are in the text; and some entries are confusing; the chemical firm Bayer, for example, is found under "Farbenfabriken Bayer".

The book is divided into fourteen chapters, some relatively short describing Haber's forebears, his youth, education, and private family life. Lengthy chapters are devoted to coverage of his Karlsruhe days, where he developed the fixation of nitration; his time before and after WW I as director of the Institute for Physical Chemistry and Electrochemistry at the Kaiser-Wilhelm Institute in Berlin; his key role in chemical warfare in WW I; and the awarding of the Nobel Prize in 1918. The author concludes with the purging of Jewish scientists from Haber's institute and elsewhere in Germany, his resignation in October, 1933, and his death from heart disease in January, 1934.

Stoltzenberg has produced a rich documentary of Haber and his era, but he has also succeeded in painting a vivid picture of the man. The reader learns that Haber, the child of "relaxed Jews," was eventually baptized as a Christian. He was ever the loyal German and only secondarily a Jew. His early love of classics, poetry, and drama was gradually superimposed by a fascination with science. He set up a chemistry laboratory in his room. When his father forbade it, his uncle allowed him space in the uncle's quarters. As a university student he was fascinated with concepts of a deity, consciousness, idealism, realism, and logic. He expressed impatience with the pedantic teaching he experienced briefly in Heidelberg under Bunsen, then 76 years old. Haber respected his colleagues throughout his life and maintained warm camaraderie with his students through regularly planned colloquia and social events. Willstätter was his life-long, closest friend. He corresponded familiarly with Einstein for a certain period of time before WW I. Always a prolific correspondent, he sometimes composed poetry to suit the occasion. Much of the correspondence is reproduced in the text. Yet Haber was not a particularly devoted family man. He excluded his first wife, Clara Immerwahr, Ph.D. (Abegg), from being involved in his research or teaching at Karlsruhe; after her suicide, he remarried but divorced Charlotte Nathan after ten years. His oldest child, the son of Clara, committed suicide in 1946.

Haber was an imaginative researcher and excellent administrator, politically very skilled, and intensely devoted to his profession. Among Haber's scientific contributions, the author describes in detail his ammonia synthesis from nitrogen, the development of electrochemistry, and luminescence. His dedication to his country is verified through his all-out effort to develop war gases, meticulously documented in Chapter 7. It also demonstrated his management skills, for he involved many scientists from the K-W Institute, some of whom served as guinea pigs, working at testing sites, designing gas masks, etc. Among them: Hahn, Geiger, Franck, Wieland, Friedländer, and Freundlich. Every one of the K-W chemical institutes was devoted fully to the war effort, except the Hahn/Meitner radium research program. Even Warburg's Biological Institute was taken over. Yet as the war proceeded, he also headed an extensive research program for the use of poison gases in pest control; he simultaneously turned his attention to the manufacture of nitrate fertilizers from ammonia, working closely with Emil Fischer. He was very adept at collaborating with German chemical industries in all these endeavors. Haber became consumed by his chemical warfare responsibilities, to the neglect of his family and friends and any earlier research interests. In the period after WWI, Haber was open to new ideas such as the quantum theory and directed research programs accordingly. Yet he could be scientifically naïve, giving support to projects on extracting gold from seawater and transforming mercury into gold. Later he absolved himself of any identity with the latter.

Stoltzenberg has accomplished what Jaenicke aspired to do at the highest possible scholarly level. More than just a carefully documented biography, this account provides insight into the scientific, social, and political events in Germany in the first quarter of the 20th century. Historians in widely diverse disciplines will recognize it as an invaluable document. An abbreviated edition in English will be published by the Chemical Heritage Foundation in 2000. Paul R. Jones, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1005.
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